IMPERIAL INSTITUTE
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PROCEEDINGS

OF THE

ROYAL SOCIETY OF LONDON

SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND
PHYSICAL CHARACTER.

VOL. CXLIII.

LONDON:
PRINTED FOR THE ROYAL SOCIETY AND SOLD BY
HARRISON AND SONS, LTD., ST. MARTIN'S LANE
PRINTERS IN ORDINARY TO HIS MAJESTY.

FEBRUARY, 1934.

LONDON:
HARRISON AND SONS, LTD., PRINTERS IN ORDINARY TO HIS MAJESTY,
ST. MARTIN'S LANE.

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ERRATA.

Paper by B. F. J. SCHONLAND and H. COLLENS, on "Progressive Lightning." 'Proceedings,' A, vol. **143**, p. 654 (February) 1934.

p. 656 :—

§ 4, 1st line, *delete* " in figs. 2 and 3 and ".

1st line of second paragraph, *for* " Figs. 2 and 3", *read* " Figs. 4 and 5 ".

1st line of third paragraph, *for* " Figs. 4 to 9", *read* " Figs. 6–11 ".

Bottom line, *for* " fig. 6, Plate 6," *read* " fig. 8, Plate 7 ".

p. 657 :—

1st line of 5th paragraph, *for* " figs. 2, 3, 4, and 5 ", *read* " figs. 4, 5, 6, and 7 ".

PROCEEDINGS OF
THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

Flame Speeds during the "Inflammation" of Moist Carbonic Oxide-Oxygen Mixtures.

By WILLIAM A. BONE, D.Sc., F.R.S., and J. BELL, B.Sc., D.I.C.

(Received July 28, 1933.)

[PLATE 1.]

In a paper communicated to the Society three years ago by one of us (W. A. B.) and Fraser it was concluded that the maximum flame-speed in both the initial (*i.e.*, the inflammation) and the final (*i.e.*, detonation) phases of explosions of moist mixtures of carbonic oxide and oxygen is attained when the composition of the medium is approximately $75CO/25O_2$.*

So far as "detonation" is concerned, this conclusion has recently been supported by the results of two series of experiments by Campbell, Whitworth, and Woodhead,† whose observed maximum rates of detonation were for mixtures containing in the first series between 77·6 and 79·7 and in the second 75·2% of carbonic oxide, although their "peak" was not so pronounced as that observed in Bone and Fraser's experiments. Moreover, they differed from the late H. B. Dixon‡ in finding no difference in velocity between "dry" and "moist" mixtures, a point of importance which now needs re-examination.

As regards the initial stage of inflammation, however—where unquestionably the flame-speed is greatly dependent upon the moisture content of the medium—the said conclusion has been challenged by Payman and Wheeler§ who from experiments with "moist" (*i.e.*, saturated at 13·1° C.) mixtures ignited at the open end of a glass tube 2·5 cm. internal diameter and 126 cm.

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* 'Proc. Roy. Soc.,' A, vol. 130, p. 542 (1930).

† 'J. Chem. Soc.,' p. 59 (1933).

‡ 'Phil. Trans.,' A, vol. 184, p. 110 (1893).

§ 'J. Chem. Soc.,' p. 1835 (1932).

long, the other end being closed, aver that "*the maximum speed of uniform movement of flame . . . is obtained with a mixture corresponding closely to* $2CO + O_2$."

Moreover, Payman and Wheeler consider such initial flame-speeds as having fundamental significance. Seeing, however, that in such circumstances the observed flame-speed for a given explosive medium is merely the resultant of the speeds of the forward movement of the flame and of the backward flow of the burnt gases escaping from the open end of the tube, it cannot be so regarded. Indeed, it seems to us that the conventional "speed-composition curves" for initial flame movements through mixtures of inflammable gases and oxygen (or air) at some specified temperature and pressure, however useful they may be, can have empirical value only relative to the particular environmental conditions involved. Moreover, it may be doubted whether, strictly speaking, the initial flame movement in any particular circumstance is of more than approximate uniformity, or its speed more than approximately constant.

Nevertheless, seeing that such curves are of practical use, and that a knowledge of the position of the maximum flame-speed in the explosive range of mixtures of any given inflammable gas with oxygen (or air) may be of theoretical interest, after reading Payman and Wheeler's paper we decided to submit the matter of the initial flame-speed in explosions of moist carbonic oxide-oxygen mixtures to a thorough re-investigation by the usual photographic method, the results of which are embodied in this paper. It will be seen that, besides confirming previous conclusions of Bone and Fraser as to the point of maximum flame-speed, these further experiments have shown the importance, not only of accurately controlling the hygroscopic condition of the media concerned, but also of ensuring a sufficient difference between the temperature of their saturation and that of the tube walls. For in absence of the latter precaution the true maximum point on the speed-composition curve may be masked or even obliterated by irregularities, especially as it is never very pronounced.

Since in making comparative measurements of initial flame-speeds of carbonic oxide-oxygen mixtures, accurate control and knowledge of their hygroscopic state is of first importance, it is usual to saturate the mixtures with water vapour at some selected constant temperature. Also, each mixture is usually ignited, by means of a small flame of constant dimensions, at the *open* end of a horizontal glass tube, whose length and internal diameter are kept constant throughout the whole series of experiments, the other end being closed.

Bone and Fraser, using such a tube 126 cm. long and 2·5 cm. internal diameter, first thoroughly evacuated (for 10 minutes down to 0·1 mm.), and then filled with the CO-O_2 mixture saturated at 12·5°. This was subsequently ignited by gently applying a 2 cm. high coal gas flame, and the results given in Table I were obtained.

Table I.

% CO in mixture	20	30	40	50	60	70	80	90
Initial flame-speed, cm./sec.	25·2	60·2	97·5	145	165	177	192	90

Indicating a point of maximum flame-speed somewhere (undetermined) between 70 and 80%, but probably nearer the latter than the former.*

Payman and Wheeler, using a tube of same dimensions, and mixtures saturated at 13·1°, admitted into the evacuated explosion tube in a fine stream through a bubbler containing water, obtained the following consistently higher flame-speeds for corresponding mixture compositions :—

Table II.

% CO in mixture	59·5	64·5	66·1	69·0	73·9	79·8
Av. Initial flame-speed, cm./sec.	234	241	250	242	230	215

From which it was concluded that the theoretical $2CO + O_2$ mixture has the maximum flame-speed.†

As bearing upon such results, our attention was directed to the following "explosion times" (t_{ms})—*i.e.*, from commencement of rise to attainment of maximum pressure—and maximum pressures (P_{ms}) observed by Fenning and Tizard when various moist CO-O_2 media (H_2O content = 1·06%) were fired centrally by means of a 0·5 mm. spark at 50° C. and 3·9 atmospheres initial pressure in a closed steel explosion vessel 7 inches diameter by 8 inches long.‡

Table III.

Ratio CO/O_2 in medium	1·26	1·53	1·99	2·39	2·92	4·37
t_{ms}, millisecs.	16	15·5	15	14	16	18·5
P_{m}, atmospheres	34·5	34·85	34·9	34·8	34·6	33·3

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* *Loc. cit.*, p. 543

† *Loc. cit.*, p. 1837.

‡ 'Proc. Roy. Soc.,' A, vol. 115, p. 327 (1927).

These indicate not only an almost constant mean maximum flame-temperature, and therefore probably average flame-speed, over a wide composition-range (*e.g.*, CO/O_2 1·26 to 2·92 inclusive), but also considerable CO_2-dissociation at the maximum temperature in each case. *Indeed, in explosions of* $2CO + O_2$ *mixtures under such conditions the percentage* CO_2*-dissociation at* P_m *is something like 40.* And, although the temperatures attained in explosions in closed vessels would be much higher than those of the corresponding flames in open tubes, yet in these latter also the degree of CO_2-dissociation would certainly be high, and on thermal grounds alone there seems no very strong *a priori* reason why the maximum temperature and flame-speed should be precisely at the $2CO + O_2$ composition. On the contrary, one would rather expect it to be with a mixture containing excess of carbonic oxide. As, however, the matter can only be settled experimentally, we will now describe our recent re-examination of it.

EXPERIMENTAL.

I.—*Initial Flame-speeds after "Open-end" Ignition in Horizontal Tubes.*

Preliminary Work.—(1) Further consideration of the experimental conditions under which the flame-speed measurements were made by Bone and Fraser and Payman and Wheeler, respectively, convinced us that no explanation of the marked difference between them could be derived from any likely difference between either the purity of the components or the moisture contents of their mixtures as and when admitted into their respective explosion tubes. Nor did it seem ascribable to any difference between the modes of ignition employed, which indeed were substantially the same in both cases. Therefore we had to look elsewhere, and it occurred to us that possibly some difference arising either during or subsequent to the evacuation of the tubes might partly account for the disagreement in question.

Such an explosion tube might, for instance, be filled with the saturated experimental mixture either (*a*) simply by displacement, when the inner wall of the tube would become covered with a film of moisture which would subsequently be added to that in the saturated medium when the flame passed along the tube, or (*b*) after a more or less prolonged evacuation during which some or all of the film of moisture usually adhering to the inner wall of the tube would be removed, so that on afterwards admitting and igniting the saturated experimental mixture the amount of moisture actually present in the resulting flame front might vary according as the prior evacuation had been short or prolonged. Hence, while the actual moisture content of the flame front would presumably in (*a*) exceed, in (*b*) it might even be less than, that calculated from the saturation temperature of the mixture.

On putting the matter to an experimental test, the foregoing anticipations were fulfilled. Thus, for example, the initial flame-speed observed on igniting a $2CO + O_2$ medium containing 10 mm. water vapour at 16·5° and 757 mm. in the usual manner at the open end of a horizontal glass tube (length 100 cm. internal diameter 2·5 cm.), the other end being closed, was found to be 220 cm. per second when the prior filling had been according to (*a*) as compared with 194 cm. only per second when it had been according to (*b*). Moreover, in a quartz tube of similar dimensions, the same moist $2CO + O_2$ mixture gave initial flame-speeds of 195 and 176 cm. per second respectively, according as the filling had been by (*a*) or (*b*).

Hence it seems possible that, unless special precautions were taken to ensure precisely the same " filling " conditions—both as regards the method employed and, in method (*b*), the length of the prior evacuation—two different observers might record different initial flame-speeds for a given CO-O_2 mixture although admitted to the tube in the same hygroscopic condition in both methods.

(2) Consequently, we decided not only to ensure more accurate control, as will be described later, of the moisture-content of our CO-O_2 mixtures, as and when admitted to the explosion tube, but also so to standardize and control their admission to the explosion tube that in each determination (i) the tube would first of all be evacuated for 2½ minutes, during which the pressure in it was reduced down to below 0·1 mm. as tested by a " discharge tube " connected therewith, and (ii) the moist (saturated at 15°) gaseous mixture would then be admitted slowly (30 seconds) after which an interval of 2 minutes would be allowed before ignition.

(3) Notwithstanding all such precautions, however, the results of several series of experiments carried out between May and July, 1932, were more or less discordant in the sense that while a series of successive flame-speed measurements with a particular moist mixture (saturated at 15° C.) made on one day would generally agree among themselves, as also would a second such series on another day, the two series did not always agree with one another. Moreover, such disagreement was far greater than could possibly be ascribed to any difference in barometric pressure on the two days concerned. Finally, after much search, it became apparent that the most likely variable factor affecting the results was the difference of temperature between that at which the moist mixture had been saturated (15° C.) and that of the room at the time at which it was ignited in the tube. This is exemplified by the flame-speed measurements

given in Table IV, obtained on different days for a $65CO/35O_2$ mixture saturated at 15° C.

Table IV.—Observed Flame-speeds for a Moist $65CO/35O_2$ Mixture Saturated at 15° C.

Date.	Barometer.	Room Temperature, ° C.	Actual speed measurements, cm. per sec.	Mean cm. per sec.
July 11, 1932	759·9	24·0	236, 236, 236, 237, 257	236
July 6, 1932	763·3	20·8	213, 217, 221, 219, 221, 216, 223	219
July 20, 1932	767·0	17·8	208, 193, 195, 201, 195, 205	201
July 25, 1932	760·3	16·0	187, 189, 189, 193, 191	190

Moreover, the point of maximum flame-speed for a series of moist CO/O_2 media (saturated at 15° C.) apparently varied with the temperature difference referred to, being *circa* $3CO + O_2$ (*i.e.*, as observed by Bone and Fraser) when the temperature of the walls of the tube was about 10° higher than the saturation temperature of the media, but becoming irregular and apparently veering towards $2CO + O_2$ (*i.e.*, as observed by Payman and Wheeler) when the temperature difference in question was less than 5° C. In neither series of experiments, however, was the maximum very marked.

It thus became evident how important it is in flame-speed measurements with moist CO/O_2 mixtures to maintain a sufficient difference (not less than about 10° C.) between the saturation temperature of the medium and the walls of the evacuated explosion tube in order to minimize any possible abstraction of moisture from the medium on admission thereto.

Final Experiments with Moist $CO\text{-}O_2$ *Mixtures* (*saturated at* 15° *C.*, $H_2O = 12{\cdot}8$ *mm.*).

We next proceeded to make three final series of flame-speed measurements with a range of moist (saturated at 15° C.) CO/O_2 media containing between 55 and 82·5% of carbonic oxide in which the utmost precautions were taken to ensure (*a*) a constant " saturation " temperature of 15° C. ($H_2O = 12{\cdot}8$ mm.) by accurately making up the experimental mixtures in mercury-sealed steel-belled gas holders, with a layer of distilled water always above the mercury, immersed in a tank of water—the temperature of which was thermostatically controlled to within + or − 1/10th°, the mixtures being allowed to remain therein for at least 16 hours before use; (*b*) in each experiment a constant period and degree of evacuation of the tube (namely, 2½ minutes by means of a Hyvac pump down to 0·1 mm. in each experiment) before admitting the experimental mixture to it; and (*c*) always a sufficient constant difference between the saturation temperature of the medium and that of the explosion tube. Special precautions were also taken to ensure the purities of the carbonic oxide and oxygen used in making up the experimental mixtures, whose compositions were always checked by analyses, and nitrogen contents always kept between 0·3 and 0·5%.

The Explosion Tube.—As shown in fig. 1, the horizontal glass explosion tube EE (1 metre long and 2·5 cm. internal diameter)—stoppered at the far end with an indiarubber bung but provided with a suitable flanged admission mouthpiece at the other—was mounted and enclosed in a rectangular wooden box (1·35 metres long × 45 cm. wide × 45 cm. high), the temperature of which could be kept constant (within ± 0·1°) by means of a combination of fans FF, heating elements HH, and mercury-toluol thermo-regulators—at any desired point above the saturation temperature of the experimental mixture. Any possibility of the flame-speeds being affected by vibratory movements set up by the fans was eliminated by stopping the latter 2 minutes before the ignition of each mixture.

Procedure.—The temperature of the explosion tube having been maintained for at least an hour at the desired point (*circa* 25, 35, or 45° C. respectively in the three series), it was next evacuated as aforesaid, whereupon the moist experimental mixture (saturated at 15° C.) was slowly admitted to it (during 30 seconds) from the holder up to slightly over atmospheric pressure. The gaseous medium was then allowed to stand for 2 minutes in the tube, after which the glass mouth-

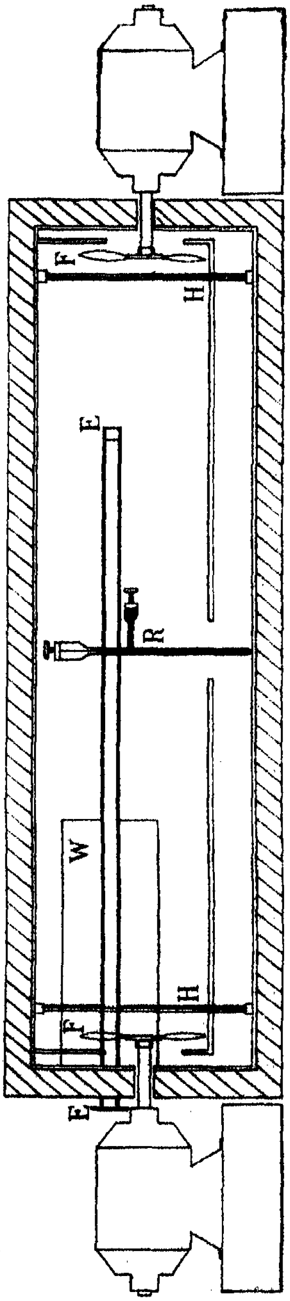

FIG. 1.

piece at the flanged end was gently removed and immediately thereafter the medium ignited by a flat 3 cm. high coal-gas flame. The resulting flame movement was photographed through a window, W, fig. 2, over a 30 cm. run (the first 5 cm. being excluded) on a film attached to the camera drum rotating at constant vertical speed of 0·6 metre per second. From the resulting photograph, which showed the flame movement to have been substantially uniform throughout the run concerned, its speed was subsequently calculated. We estimate that the probable measurement error involved would not exceed ± 2·5%, or, say, ± 5 cm. per second in any individual measurement.

Commencing, in each series of experiments, with a $55CO/45O_2$ medium, a number of flame-speed measurements were first made at each of several consecutive points along the explosion-range until well past the $80CO/20O_2$ composition, after which the range was again traversed by similar measurements, but in the reverse order, so that the range was always twice covered in each series. Moreover, a number of individual measurements (never less than four and sometimes more than ten) were always made at each selected point up or down the explosive range so covered. Each group of determinations was completed within 3 hours, and the resulting photographs all developed together; but the flame-speeds were not calculated therefrom until after the whole series of experiments had been completed.

Details of all such flame-speed measurements in each series, including the order of each group concerned, are shown in Tables V, VI, and VII, respectively, from which it will be seen that a fairly close agreement is shown between the great majority of individual measurements in each such group. Occasionally an individual result (shown within brackets in the tables) showed a divergence of more than ± 10 cm. per second from the mean value for each group, which is more than could possibly be accounted for by experimental error. Such abnormal values were regarded as accidental and were accordingly ignored in calculating the mean flame-speed in each group; in no case, however, did this affect the general conclusion as to the point of maximum flame-speed in each series. Moreover, seeing that the proportion of such abnormal results diminished, and eventually disappeared, as the temperature difference between the walls of the explosion tube and the saturation point of the moist medium was increased—being 17 out of 96 measurements when the difference referred to was about 10°, 2 only out of 92 measurements when it was about 20°, and none at all out of 79 measurements when it was 30°—they would seem to have arisen from occasional slight irregularities in moisture-interchanges between tube walls and the gaseous medium which were eventually eliminated when the temperature difference between them was sufficiently increased. It will be seen that, as formerly observed by Bone and Fraser, in each of the three series of experiments the maximum flame-speed was obtained with a medium *circa* $75CO/25O_2$. The fact that as a whole our observed flame-speeds were consistently higher than theirs at corresponding mixture compositions is

Tables V–VII.—Observed Initial Uniform Flame-speeds for "Moist" CO/O_2 Media (saturated at 15·0° C.) in a horizontal tube 1 metre long and 2·5 cm. internal diameter.

V.—Tube walls maintained at 24·0° C.

Group order.	CO in medium %	Barometer mm.	Actual flame-speed measurements, cm. per sec.	Mean flame-speed, cm./sec.
13	55·0	761	230, [216], 222, 225, 227, 227, 227	226
1	55·2	755	220, [208], [199], 233, 235, 228, 231	230
2	60·0	755	238, 239, 229, 230, 229, 233	235
12	60·2	762	[254], 236, [219], 233, 235, [220], 238, 235, 239, 236, 244	237
3	65·1	755	[253], 233, 229, 233, 232, 230, 235	232
11	66·7	762	246, 243, [230], [263], 241, 241, 242, 244, 241	242
4	70·7	757	253, 257, 260, 258	257
10	71·3	764	[285], 256, 255, 256, 257, [235], 250, 245, 256	254
5	75·1	763	265, 266, [233], 247, 264	261 } Max
9	75·7	766	259, 264, [200], 267, 264, [280], 252, 253	260 }
8	77·5	765	256, 253, 256, [230], 261, 251, 256	255
7	79·6	765	239, 247, 234, 236, 243, 236, 238	239
6	80·5	763	[226], 248, 234, [251], 240, 230, [210], 236, 244	240

VI.—Tube walls maintained at 34·7° C.

Group order.	CO in medium %	Barometer mm.	Actual flame-speed measurements, cm. per sec.	Mean flame-speeds cm. per sec.
2	55·0	768	220, 210, 221, 224, 219, 218	219
1	55·4	767	217, 219, 217, 220, 221, 222, 223, 226, 210, 225	219
3	64·8	762	232, 234, 234, 234, 229, 223, 233, 236, 225, 236, 236, 236	232
10	66·0	764	231, [220], 245, 233, 240, 240, 240, 236, 237	238
4	67·5	762	235, 235, 236, 233, 235, 236	235
7	70·5	760	252, 248, 252, 264, 253, 253, 255, 253	252
8	75·1	760	254, 252, 252, 255, 257, 256, 255, 260, 254, 256, 265	256 Max.
9	78·4	764	240, 231, 245, 242, 244, 242, 238, 235, 235, 240, 240, 238	239
6	81·1	750	206, 203, [192], 201, 204, 201, 204, 206, 203	203
5	82·5	750	183, 184, 199, 184, 190 ,190, 199, 190	191

VII.—Tube walls maintained at 46·6° C.

Group order.	CO in medium %	Barometer mm.	Actual flame-speed measurements, cm. per sec.	Mean flame-speeds, cm. per sec.
3	55·0	748	216, 216, 217, 216, 216, 214, 218, 218	216
1	55·7	770	214, 224, 215, 216, 219, 217, 215, 217, 214, 214	216
4	60·0	749	234, 236, 234, 233, 240, 233, 240	234
8	62·5	759	237, 240, 236, 240, 239, 232, 242, 241, 239, 239	239
2	63·2	770	240, 238, 238, 238, 238, 237, 237, 235	238
5	65·4	746	240, 240, 235, 240, 239, 236, 238, 240, 242	240
9	66·3	761	244, 236, 237, 240, 244, 235, 235, 240, 240, 242	240
6	70·9	746	251, 251, 249, 251	251
10	75·0	761	260, 260, 259, 258, 258	259 Max.
7	80·6	752	213, 216, 213, 217, 216, 216, 218	216

probably mainly due to the somewhat higher moisture content of the media used in our experiments as compared with theirs (*i.e.*, 12·8 mm. as compared with 11 mm.). Moreover, so far from the maximum flame-speed being at the $2CO + O_2$ composition, as Payman and Wheeler have asserted, there was actually a tendency for a "hollow" in the speed-composition curve (*vide* fig. 2) in such region. Indeed the general character of the curve is much as might be expected were the suppression of CO_2-dissociation by excess of either CO or O_2, respectively, an important factor in regard to the relative flame-speeds.

It may also be noted how nearly the flame-speeds at corresponding mixture compositions came out the same in the three series (*e.g.*, for the $3CO + O_2$ medium they were 261, 259, and 256 cm. per second) showing how little they had been affected by the successive falls in the density of the medium as its temperature was raised from 24° to 35° and finally to 46·6°. Clearly, then, "moisture-content" was the governing factor in regard to the order of the flame-speeds of CO_2-O_2 media within the temperature range involved.

Experiments with "Semi-dried" CO-O_2 *Media.*

We next essayed, using the same apparatus and method, to determine the effect upon the flame-speeds of considerably drying the CO-O_2 media, and for this purpose they were partially dried by overnight storage at 24° over a 57·6% aqueous sulphuric acid, which would reduce their moisture content to 4·8 mm. (corresponding with "saturation" at 0·8° C.) as compared with 12·8 mm. in the previous three series. The temperature of the explosion tube was kept between 21° and 24°, or sufficiently high to prevent any condensation of moisture on its walls when the so-dried mixtures were introduced into it. In all other respects (*i.e.*, except in regard to the partial drying of the mixtures in the present experiments) the experimental procedure was unaltered. The results, which are detailed in Table VIII, showed, as was expected, a great general reduction in the observed flame-speeds at corresponding points, as compared with those observed in the previous three series with the "saturated" media. And although the proportion of "abnormal" speed measurements

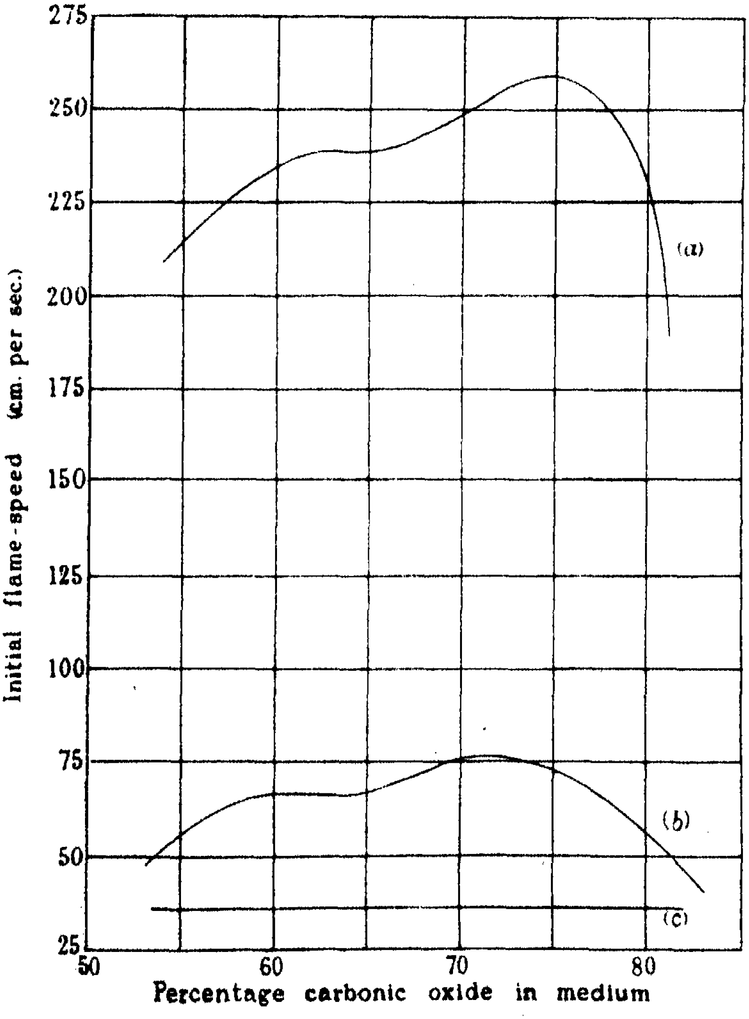

FIG. 2.—(*a*) CO-O_2 media containing 12·8 mm. water vapour; (*b*) CO-O_2 media containing 4·8 mm. water vapour; (*c*) CO-O_2 media dried over calcium chloride.

was larger than before (15 out of 90 measurements being rejected under our rule), the results now showed a marked maximum flame-speed at the $70CO/30O_2$ point, or about mid-way between the $2CO + O_2$ and $3CO + O_2$ compositions. Here again there was a distinct tendency towards a "hollow" in the speed-composition curve (*vide* fig. 2) in the neighbourhood of the $2CO + O_2$ point.

Table VIII.—Observed Initial "Uniform" Flame-speeds with "Semi-dried" CO-O_2 Media. Moisture content = 4·8 mm. Tube temperature = 24° C.

Group order.	CO in medium %	Barometer mm.	Actual flame-speed measurements, cm. per sec.	Mean flame-speeds cm. per sec.
8	55·5	777	58·7, 58·7, 57·7, 56·5, 56·5, 60·8	58·1
11	59·6	776	68·7, 63·1, 67·8, 67·1, 65·2	66·4
2	62·6	762	68·7, 69·2, 64·6, 65·8, 67·3, [62·5], 68·2, 65·0	67·0
1	62·9	758	67·1, 65·9, [61·7]	66·5
12	63·2	772	66·5, [60·0], 67·1, [70·0], 67·1, 63·5	66·1
10	63·2	775	[69·3], 66·7, 66·7, 64·7, 64·7, [62·8]	65·7
4	64·7	765	65·9, 65·0, 62·2, [61·5], [58·9], [60·7], 64·6, 64·9	64·5
13	65·0	772	64·7, 67·3, 65·5, 69·8, 66·8, [61·7], 66·7, 69·7	67·2
5	67·7	765	69·0, 68·9, 73·7, 70·5, 74·0, 74·4	71·7
3	69·9	762	74·5, 75·3, 77·2, 79·2, 73·1, 74·8	75·7 max.
9	71·7	776	72·3, [82·9], [79·6], 71·6, 71·6, 72·4, 71·8	71·9
7	76·3	767	67·9, 69·7, 67·8, 72·3, 67·4, 69·2, 70·8	69·3
14	80·3	763	54·9, 52·5, 54·9, [61·0], 53·1, 58·2, 55·8, [60·0]	55·0
6	80·4	768	55·3, [62·2], 53·6, 53·7, 53·7, [59·2]	54·1

Experiments with $CaCl_2$*-dried* CO-O_2 *Media.*

In order to make our investigation as complete as possible on the point at issue, we finally experimented, in a similar manner as before, with a series of mixtures which had been well dried by passage over a 2 metres long column of calcium chloride so as to reduce their moisture content to *circa* 0·03%. The results, which are detailed in Table IX, showed a further great reduction in the initial flame-speed, but little variation from 35 cm. per second throughout the whole composition range (55 to 80% CO) examined. Certainly no maximum point could be detected, the speed-composition curve (fig. 2) being now a nearly horizontal line, thus simulating the results of Fenning and Tizard's experiments, in which much the same range of moist CO-O_2 media were exploded *under pressure* in a closed steel vessel. And the similarity probably means (as already amply proved by numerous previous investigations) that *under pressure* carbonic oxide burns mainly *without the intervention of steam.*

II.—*Initial "Uniform" Flame-speeds when a Moist* $2CO + O_2$ *Mixture is ignited near the closed end of a Horizontal Tube, the other end being open.*

Seeing that, as already stated in our introduction, the observed initial flame-speed when a given inflammable gaseous medium is ignited at the *open* end of a horizontal tube, which is closed at the other, can only be the *resultant* of two opposite speeds (*i.e.*, of the *forward* movement of the flame and the *backward* flow of the escaping products)—it seemed of interest to ascertain what would be the order of the real initial uniform flame-speeds forwards in, say, a moist $2CO + O_2$ mixture when unopposed by such backward flow of products.

The experimental determination of such speed is not an easy matter, because not only has it been found necessary for ignition to occur very near the *closed* end of a tube, but also to ensure the medium remaining substantially stagnant during the ensuing flame propagation.

Table IX.—Observed Initial Uniform Flame-speeds in Calcium Chloride dried CO/O_2 Media. Tube temperature = 17 to 20° C. (room).

CO in medium %	Observed flame-speeds, cm. per sec.	Mean flame-speeds, cm. per sec.
54·7	35·5, 37·2, 34·6, 34·2, 35·6, 33·8, 35·5	35·2
62·6	37·6, 36·1, 35·7, 37·0	36·7
66·4	33·3, 33·9, 33·9, 34·8, 34·1, 36·6, 36·3, 35·6	34·8
67·1	37·0, 34·8, 36·0, 35·0, 38·3, 36·7	36·3
70·3	33·8, 35·9, 33·0, 33·3, 33·0, 33·8, 33·0, 32·5	33·5
70·9	35·7, 34·0, 36·0, 33·9, 34·5, 34·4, 36·0	34·9
74·7	37·4, 35·7, 37·1, 37·0, 37·0, 36·5, 36·5, 37·3, 37·6	36·9
75·0	33·7, 33·5, 33·0, 33·0, 34·7, 35·9, 35·7, 36·0, 34·5	34·7
77·9	37·0, 37·0, 34·2, 37·3, 37·1, 37·1, 35·3	36·5
79·2	36·6, 34·1, 35·6, 35·8, 37·1, 35·5, 37·5	36·0

Bone and Fraser, who first dealt with this point, and published an experiment thereon (*q.v.*) in connection with their photographic researches on flame movements in gaseous explosions, found that the requisite conditions can be obtained with a moist (saturated at 18°) $2CO + O_2$ medium by igniting it by means of a heavy condenser discharge (0·0065 m.f. at 10,000 volts = 0·325 Joule) at a point 0·5 cm. only from the *closed* end of a horizontal explosion tube (internal diameter = 1·25 cm. and length = 1·5 metres) the other end of which was open. In this way any compression waves set up by the spark passed through and out of the explosive medium far ahead of the much more slowly moving flame, and the resulting flame-photograph showed that, while a long initial phase of practically uniform flame-speed of 30 metres per second resulted, the medium through which it passed remained practically stationary throughout the experiment. Such speed was some 13 times greater than that observed when the same moist $2CO + O_2$ medium was ignited near the open end of the tube, the other end being closed, showing how overwhelming (in the latter case) is the influence of the opposite flow of escaping products.*

On pursuing the matter further with a moist $2CO + O_2$ (saturated at 12°) medium, we succeeded in firing it near the *closed* end (*a*) of a horizontal glass tube 1·5 metre long and 1·3 cm. internal diameter, by means of a condenser discharge of 0·1 m.f. at 12,000 volts, the room temperature being 20·5° and barometer 769 mm., and (*b*) of a similar tube 6·3 metres long and 2·5 cm. internal diameter, by means of a discharge of 0·2 m.f. at 12,000 volts, the room temperature being 14° and barometer 768 mm. In each experiment the other end of the tube was opened immediately before firing.

The resulting photographs,† figs. 3 and 4, Plate 1, show in fig. 3 a long initial and nearly uniform flame-speed of 60 metres per second and in fig. 4, a much shorter but still nearly uniform initial flame-movement of 69 metres per second, the medium remaining practically stagnant while the flame-front passed through it. The fact that the speed observed in fig. 3 is about double that observed in a similar experiment by Bone and Fraser, in which a less heavy condenser discharge was used as the source of ignition, suggests that the initial flame-speed set up under such conditions depends upon the energy of the discharge. Be that as it may, however, such initial uniform flame-speeds in a substantially stagnant moist $2CO + O_2$ (saturated at 12°) medium, in circumstances precluding escape of combustion products, should be compared with the approximate 2·5 metres per second (Tables V to VII) observed when the same medium (but saturated at 15°) was ignited at atmospheric pressure near the *open* end of a horizontal tube (closed at the other end) involving their escape.

It is evident that these results finally dispose of the claim, so often put forward, that the initial uniform flame-speed observed when an explosive medium is ignited in the conventional manner at the *open* end of a horizontal tube, the other end of which is closed, can be regarded as having any fundamental significance.

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* 'Phil. Trans.,' A, vol. 230, pp. 367–9 and Pl. 13, photograph No. 1 (1932).

† Taken in the usual manner on a film moving vertically at constant velocity (7·3 metres per second), the flame movement being horizontal.

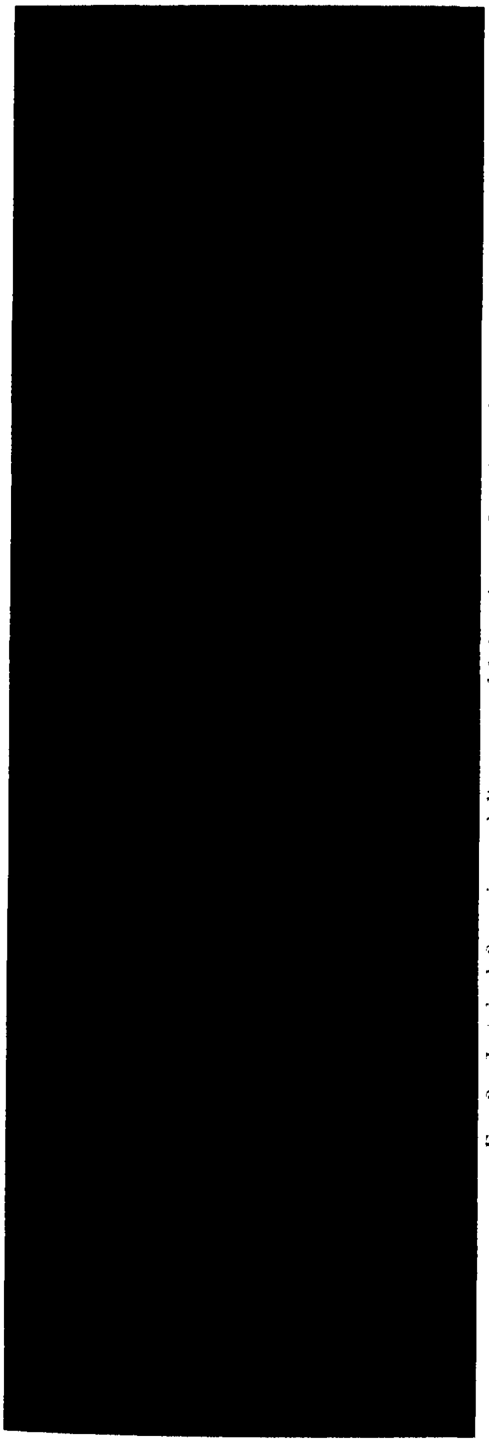


Fig. 3.—In tube 1·3 cm. internal diameter and 1·5 m. long. Initial speed 60 m./sec.

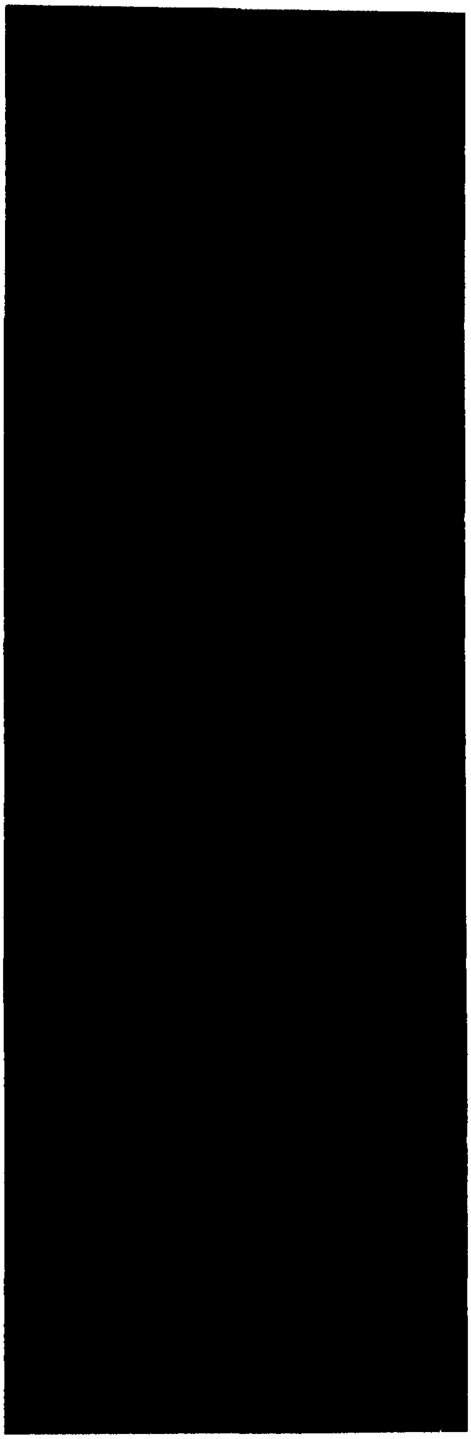


Fig. 4.—In tube 2·5 cm. internal diameter and 6·3 m. long. Initial speed 69 m./sec.

Flame propagation following the ignition of moist $2CO + O_2$ mixtures near the closed end of a horizontal tube, the other end being open.

In conclusion, we desire to acknowledge our indebtedness to the Gas Light & Coke Company, London, for a Research Fellowship which has enabled one of us (J. B.) to devote his whole time to the work.

Summary.

I.—It has been shown (*inter alia*) that, when successive CO-O_2 media within the 55CO/45O_2 and 80CO/20O_2 range are gently ignited at atmospheric pressure at the open end of a horizontal glass tube, the other end of which is closed, and when all due precautions are taken to ensure accurate measurements :—

(1) With moist media, saturated at 15°, the maximum initial "uniform" flame-speed is attained at the 3CO + O_2 composition.

(2) Partial drying of such media tends to move the maximum flame speed-point somewhat towards the 2CO + O_2 composition, until with media containing 4·8 mm. moisture (corresponding with saturation at 0·8° C.) it is at the composition *circa* 70CO/30O_2.

(3) In no experiment, within the degree of drying referred to, is there any sign of a maximum flame-speed at the 2CO + O_2 point; on the contrary, there is always a tendency for a hollow in the speed-composition curve in that region, as though the suppression of CO_2-dissociation by excess of either CO or O_2, respectively, is an important factor in regard to the relative flame-speed.

(4) A nearly complete drying of such media by means of calcium chloride produces an almost constant initial uniform flame-speed of *circa* 35 cm. per second throughout the whole composition range in question.

II.—It has also been shown that the speed of the initial "uniform" movement set up when a moist 2CO + O_2 medium is ignited by a heavy condenser discharge near the *closed* end of a horizontal tube, the other end of which is open, may be many (*e.g.*, 15 to 30) times greater than that of the initial uniform movement when the same mixture is ignited by a small flame at the *open* end of a tube of similar diameter (the other end of which is closed) thus permitting escape of combustion products; and that the flame-speeds under the latter condition are devoid of any fundamental significance.

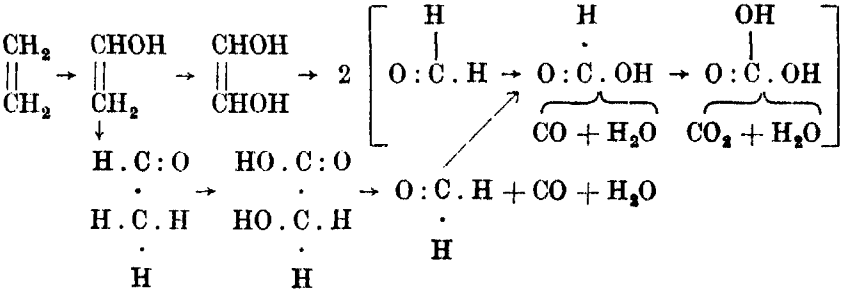
The Slow Combustion of Ethylene.

By William A. Bone, D.Sc., F.R.S., A. E. Haffner, Ph.D., and
H. F. Rance, B.Sc., A.R.C.S.

(Received July 28, 1933.)

Although much work has been done in the slow oxidation of ethylene since one of us with R. V. Wheeler discovered that it involves the intermediate formation of acet- and form-aldehydes and formic acid, without any liberation of either carbon or hydrogen, some difference of opinion has recently arisen as to the nature of the initial product.

Bone and Wheeler*—who worked with various ethylene-oxygen mixtures both in sealed bulbs at 300° to 350° and about 2 atmospheres pressure, and in their circulation apparatus in contact with porous porcelain at 400° and pressures below 500 mm.—concluded that the main course of the combustion could be represented by the following hydroxylation scheme :—



part of the unstable vinyl alcohol initially formed changing into the isomeric acetaldehyde which would then independently undergo further oxidation as indicated.

Moreover, in 1906, Bone and Drugman† showed that the explosive combustion of ethylene could also be similarly represented, thermal decomposition occurring at stages (1) and/or (2) according to the proportion of oxygen present, there being strong evidence of the initial formation of a monhydroxy-ethylene.

Experiments by Willstätter and Bommer in 1921,‡ while showing that under favourable circumstances about half the theoretical amount of formaldehyde indicated by the hydroxylation scheme can be recovered, revealed nothing as to the initial product. A year later, however, Blair and T. S. Wheeler*—who made an extensive experimental study of the subject for the Chemistry Research Board of the Department of Scientific and Industrial Research, with special reference to the maximum production of formaldehyde—showed that under certain conditions (*e.g.*, very slow reaction, induced by great excess of oxygen at 560°) as much as 50% of the ethylene burnt could be recovered as acetaldehyde and another 29% as formaldehyde, and they suggested the following slight modification of the original "hydroxylation" scheme :—

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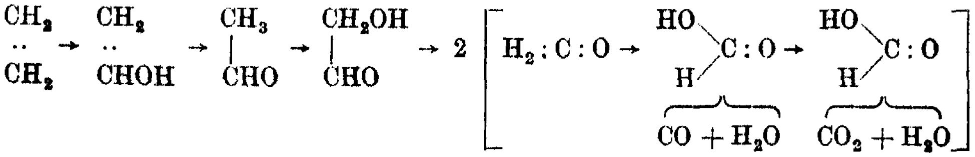
* 'J. Chem. Soc.,' vol. 85, p. 1637 (1904).

† 'J. Chem. Soc.,' vol. 89, p. 660 (1906).

‡ 'Leibigs Ann.,' vol. 422, p. 36 (1921).



$$\begin{matrix}CH_2\\ \cdot\cdot\\ CH_2\end{matrix} \rightarrow \begin{matrix}CH_2\\ \cdot\cdot\\ CHOH\end{matrix} \rightarrow \begin{matrix}CH_3\\ |\\ CHO\end{matrix} \rightarrow \begin{matrix}CH_2OH\\ |\\ CHO\end{matrix} \rightarrow 2\left[H_2:C:O \rightarrow \underbrace{\begin{matrix}HO\\ H\end{matrix}\!\!>C:O}_{CO + H_2O} \rightarrow \underbrace{\begin{matrix}HO\\ H\end{matrix}\!\!>C:O}_{CO_2 + H_2O}\right]$$

Here matters rested until, in 1929, Thompson and Hinshelwood† studied the kinetics of the oxidation in silica vessels at temperatures between 400° and 500°, and finding that the rate is affected by the total pressure approximately as in a reaction of the third order, the effect depending very much more on the partial pressure of the ethylene than on that of the oxygen, they suggested that, although "there is no doubt that Bone's interpretation of the complete course of oxidation as a process of successive hydroxylation is essentially correct, . . . the first stage in the reaction is the formation of an unstable peroxide ; if this reacts with more oxygen the chain ends, but if it reacts with ethylene unstable hydroxylated molecules are formed which continue the chain." It should be noted, however, that neither they nor indeed any others have adduced any experimental proof of the actual formation of the assumed initial peroxide.

Two years ago Lenher‡ reported (i) on passing an equimolecular ethylene-oxygen mixture through a cylindrical pyrex vessel (vol. = 65 c.c.) at temperatures between 360° and 410°, the formation of ethylene oxide, glyoxal, formaldehyde, formic acid as well as carbonic oxide and steam although, in large vessels (960 c.c.), "dioxy-methyl-peroxide" (supposedly formed by the oxidation of CH_2O with H_2O_2 produced in the reaction) appeared ; and (ii) in circulation experiments with $90C_2H_4/10O_2$ mixtures at temperatures between 410° and 600°, the formation of ethylene oxide and formaldehyde, as well as of some acetaldehyde. From these results he concluded that the oxidation probably consists of the activation of ethylene and formation of a peroxide, leading to the production of C_2H_4O, together with a direct passage from C_2H_4 to CH_2O, the other products appearing in subsequent steps. But apparently his experimental conditions allowed of side reactions to such an extent as to obscure the main course.

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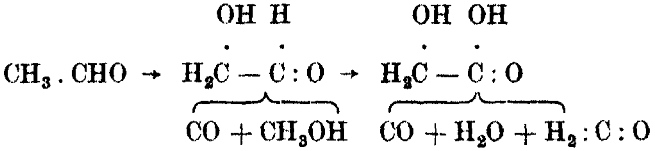
* 'J. Soc. Chem. Ind.,' vol. 41, p. 303T ; vol. 42, p. 415T (1922–23).

† 'Proc. Roy. Soc.,' A, vol. 125, p. 277 (1929).

‡ 'J. Amer. Chem. Soc.,' vol. 53, pp. 2420–1 and p. 3737 (1931).

More recently Pichler and Reder* have found methyl alcohol among the oxidation products of ethylene at high pressures, a result which, in the light of Newitt and Bloch's† work, may be attributed to an intermediate step in the further oxidation of acetaldehyde thus:—



$$CH_3 . CHO \rightarrow \underbrace{H_2\overset{OH}{\dot{C}} - \overset{H}{\dot{C}} : O}_{CO + CH_3OH} \rightarrow \underbrace{H_2\overset{OH}{\dot{C}} - \overset{OH}{\dot{C}} : O}_{CO + H_2O + H_2 : C : O}$$

In view of its importance in relation to the general theory of hydrocarbon combustion it was decided to subject the slow oxidation of ethylene to careful re-examination both at ordinary and high pressures; and this paper embodies the new results at ordinary pressures, leaving the high pressure experiments, which one of us (H. F. R.) is carrying out with Dr. D. M. Newitt, to be published later.

EXPERIMENTAL.

General.

In our re-examination of the subject we have been careful to choose experimental conditions such as, while ensuring a measurable rate of oxidation, would obviate as far as possible side-reactions and enable quantitative determinations being made of each of the principal products present at the end of the selected time intervals during the reaction period. Of the apparatus and procedure, which were substantially the same as that adopted in previous similar experiments on methane and ethane by one of us in conjunction with Allum and Hill, no more need be said than that it involved introducing various mixtures of ethylene and oxygen into an evacuated cylindrical bulb (27·5 cm. long, 5 cm. internal diameter and 586 c.c. capacity) of transparent silica, maintained at a constant temperature of 300°, and following the subsequent reaction by means of pressure records and chemical analyses, arrangements being made whereby, as and when desired, the vessel and its contents could be suddenly cooled at any moment by plunging it into a mixture of ice and water so as to stop the reaction and enable the chemical composition of the medium being exactly ascertained.

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* 'Z. angew. Chem.,' vol. 46, p. 161 (1932).

† 'Proc. Roy. Soc.,' A, vol. 140, p. 426 (1933).

Although most of the experiments were made with moist mixtures, initially containing about 10 mm. of water vapour, a special comparative series was carried out with an equimolecular $C_2H_4 + O_2$ mixture, both (*a*) P_2O_5-dried and (*b*) containing 1% or 2% of moisture, so as to ascertain precisely the effect (if any) of moisture on the oxidation. Similarly, also, the effects of small amounts of other possible reaction products (*e.g.*, ethylene oxide, acetaldehyde, formaldehyde vapours) as well as of nitric oxide, upon the "induction" and "reaction" periods, respectively, were ascertained.

Detection and Estimation of Intermediate Products.

At the conclusion of each experiment, and after a sample of the gaseous products had been withdrawn over mercury for analysis, the contents of the reaction vessel were rinsed out usually with 2 × 25 c.c., but in special estimations (*e.g.*, for the estimation of the ethylene oxide) with only 2·5 c.c., of distilled water, and the rinsings examined both qualitatively and quantitatively for soluble intermediate products as follows:—

(i) *Ethylene oxide* by adding to the aforesaid 2·5 c.c. of rinsings a saturated solution of manganese chloride and matching the precipitated $Mn(OH)_2$ formed in the cold during the next 3 days with that formed in like manner from dilute ethylene oxide solution of known strength.*

(ii) *Aldehydes.*—The total present having been estimated by means of Ripper's bisulphite method, the formaldehyde was then separately estimated by a colorimetric method, based on the suppression by means of concentrated sulphuric acid of the colour produced by higher aldehydes (but not that by formaldehyde) with Schiff's reagent. The result always showed the aldehyde to be nearly all formaldehyde. The iodoform test was also applied for the detection of acetaldehyde invariably without any precipitate of iodoform though its odour was usually in evidence, the sensitiveness being affected by the presence of other oxidation products. We made fairly sure that, though

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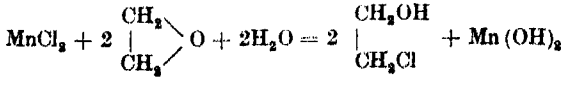
* The reaction involved is



$$MnCl_2 + 2\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O + 2H_2O = 2\begin{array}{l}CH_2OH\\ |\\ CH_2Cl\end{array} + Mn(OH)_2$$

and special trials showed that, carried out in this way, it gives approximately quantitative results.

invariably present, the partial pressure of any acetaldehyde in the gaseous products examined would not exceed 1 mm. and was practically negligible.

(iii) *Glyoxal* was detected by means of its red *p*-nitrophenyl hydrazone which, if filtered hot, can be separated from the more soluble corresponding derivatives of formaldehyde ; and the blue colour, given to the red residue with alcoholic potash, served as the basis for its colorimetric estimation. The amount so found was, however, almost negligible—its vapour pressure never exceeding 1 mm. in the total gaseous products—and everything pointed to its formation resulting from some side-oxidation.

(iv) *Acids.*—Only formic acid was ever present, and it was estimated by titration with N/50 potassium hydroxide.

(v) *Peroxides*, when detected, were estimated colorimetrically by means of a 5% solution of titanic sulphate in 5% sulphuric acid, using a N/50 hydrogen peroxide as a standard for comparison, such test being sensitive to 1 part in 500,000. In experiments in which most of the oxygen had been used up no peroxide could be detected in the end products, it being present in small amounts and only when aldehydes were being formed in presence of oxygen, and then it was calculated as $C_2H_4O_3$.

(vi) *Vinyl Alcohol.*—While control experiments had shown that the foregoing methods would suffice for the estimation of the products already referred to, no sufficiently delicate test was available for the detection of the small amounts of C_2H_4O possibly present as the unstable vinyl alcohol (monhydroxyethylene) ; its presence or otherwise could therefore only be inferred " by difference " from the carbon-hydrogen-oxygen balances for each experiment after the whole of the analytical work involved had been completed.*

Carbon-Hydrogen-Oxygen Balances.

Accordingly a C-H_2-O_2 balance was drawn up from the analytical data for each experiment showing in the first place the units of each element (i) in the original dry gaseous medium, and (ii) in the combined gaseous products *plus* condensable products more highly oxidized than C_2H_4O (*i.e.*, formaldehyde and formic acid respectively). Any residual carbon thus unaccounted for was then provisionally assumed to have been present in some isomeric form of C_2H_4O (*i.e.*, as vinyl alcohol, ethylene oxide and acetaldehyde), a supposition which was substantially verified by deducting the corresponding C-H_2-O_2 units and finding that the ratio of the residual unaccounted for hydrogen and oxygen was substantially that required for H_2O the only remaining product. Finally, after deducting from the total partial pressure of C_2H_4O so obtained the already ascertained partial pressures of ethylene oxide and acetaldehyde any residual C_2H_4O—usually one-third of the whole—was attributed to the isomeric vinyl alcohol.* The relative proportions of vinyl alcohol, ethylene oxide and acetaldehydes were usually of the order of 4 : 10 : 1.

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* [*Note added in proof, October* 16, 1933.—While this paper was in the press, however, one of us and Dr. D. M. Newitt isolated vinyl alcohol, by means of its double compound with mercury-oxychloride, from the products of the pressure-oxidation of ethylene at 240° and 50 atms. in which it is formed in relatively large amounts.]

While the last-named inference, having to bear the brunt of analytical errors, should be regarded with due reserve, it is not only consistent with the evidence as a whole, but is supported by the outstanding fact that while practically no steam (but only carbonic oxide and hydrogen) results from the explosion of a $C_2H_4 + O_2$ medium, it is abundantly formed in a $3C_2H_4 + 2O_2$ explosion, as if by the thermal decomposition of monhydroxyethylene. Moreover, on general grounds, it seems probable that any C_2H_4O vapour in the hot slow combustion products of ethylene must always be composed of its three isomeric forms in an equilibrium ratio dependent upon pressure and temperature, a point that will be reconsidered later.

General Features of the Oxidation.

The experiments described herein have all been carried out at 300° C. and atmospheric pressure. In such circumstances the slow reaction between ethylene and oxygen is substantially homogeneous, and can be stopped by packing the reaction vessel with fragments of fused silica. It is also characterized by a well-marked " induction period " during which the pressure either remains stationary or falls slightly, and this is followed by a " reaction period " during which (as we have found) the pressure first of all steadily rises until the free oxygen in the medium approaches exhaustion, after which a pressure-fall may supervene, this latter being more pronounced as the oxygen-content of the original medium is progressively reduced below the equimolecular, but ceasing when it exceeds such proportion (*vide* the pressure-time curves shown in fig. 1). This feature is consistent with the hydroxylation theory, for whereas the initial oxidation stage—the effects of which become increasingly evident as the oxygen content of the medium diminishes towards the end of an experiment—involves pressure-reduction, in a plentiful oxygen supply it is masked and overcome by the rapidity of the steam and carbonic oxide formation, involving a pressure-rise, at the third stage; for the pressure-time curve merely shows the resultant of the two opposing effects at any particular moment.

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* See note on previous page.

The chief and constant oxidation products in our experiments were C_2H_4O (*i.e.*, a mixture of vinyl alcohol ethylene oxide and acetaldehyde isomers)

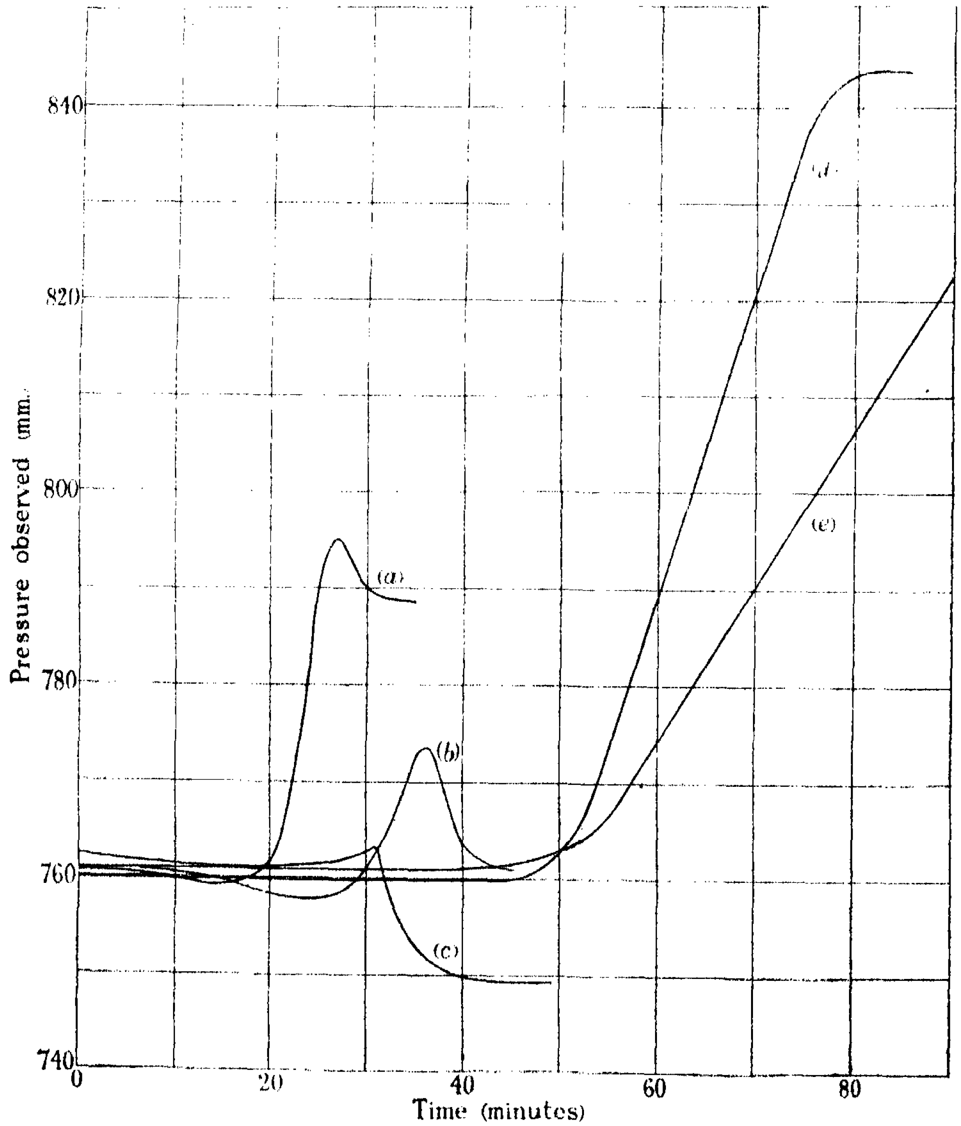


Fig. 1.—Observed pressure-time curves with various C_2H_4-O_2 mixtures. (*a*) $2C_2H_4 + O_2$ (3); $3C_2H_4 + O_2$ (2); (*c*) $5C_2H_4 + O_2$ (1); (*d*) $C_2H_4 + O_2$ (4); (*e*) $C_2H_4 + 2O_2$ (5). The numbers in brackets correspond to the numbers in Table III.

formaldehyde, formic acid, oxides of carbon and steam. Small amounts of a peroxide were also sometimes present, but never until after some accumulation of aldehydes, while hydrogen was usually absent.

Also, small amounts of ethane and/or propane were usually present, but further detailed investigation suggested their probable formation by such side reactions as (i) $C_2H_4 + H_2 : C : O = C_2H_6 + CO$ and/or (ii) $3C_2H_4 + 2H_2 : C : O = 2C_3H_8 + 2CO$, the former of which would involve no pressure-change but the latter a slight pressure-fall.

Induction and Reaction Periods.

In keeping with what had previously been observed with other substances (*e.g.*, methane or ethane) the durations of the induction and reaction periods were found to vary with the relative proportions of hydrocarbon and oxygen in the medium, and were much the shortest with a $2C_2H_4 + O_2$ mixture as shown by the following comparative figures in Table I for media containing 1% of water vapour.

Table I.

Mixture.	Duration in minutes.					
	(1) Induction.	(2) Reaction.				
		(*a*) Pressure rise.		(*b*) Pressure fall.		Total.
$5C_2H_4 + O_2$	24	7	+	13	=	20
$3C_2H_4 + O_2$	25	11	+	9	=	20
$2C_2H_4 + O_2$	16	11	+	5	=	16
$C_2H_4 + O_2$	44	36	+	0	=	36
$C_2H_4 + 2O_2$	47	330+	+	0	=	330+

The fact that excess of oxygen beyond the $2C_2H_4 + O_2$ proportion has such a marked retarding effect is of great significance, especially when considered in connection with the further observation that whereas small amounts of aldehyde vapours appear quite soon during the induction period and slowly accumulate as it proceeds, no trace of any peroxide could ever be detected until well into the reaction period, and then only after a considerable accumulation of aldehydes in the system, notwithstanding that the test employed for peroxide was even more sensitive than that for aldehyde. Indeed, this part of the evidence has greatly strengthened the results of other experiments with methane-oxygen mixtures, now proceeding in our laboratories, which have shown the induction period to depend chiefly upon the presence of small amounts of aldehyde and to a lesser extent of steam (but not at all upon peroxide) in the system.

Influences of Third Substances upon Induction and Reaction Periods.

In other comparative series of experiments the influences of small additions of various third substances upon the duration of " induction " and " reaction " periods, respectively, of a P_2O_5-dried $C_2H_4 + O_2$ medium at 300° and 760 mm. were studied, with the typical results given in Table II.

Table II.

$C_2H_4 + O_2$ medium.	Duration in minutes.					
	(1) Induction.	(2) Reaction.				
		(a) Pressure rise.		(b) Pressure fall.		Total.
P_2O_5-dried	54	37	+	13	=	50
plus						
1% H_2O	56	29	+	21	=	50
2% H_2O	48	39	+	11	=	50
1% NO	0	20	+	8	=	28
1% $CH_3 . CHO$	2	42	+	8	=	50
1% ethylene oxide	45	75	+	10	=	85
3% ethylene oxide	55	90	+	10	=	100
1% $H_2 : C : O$	25	38	+	13	=	51

The small influence of steam on either " induction " or " reaction " periods is noteworthy. Most significant of all, however, is the marked contrast between the effects of the two isomers acetaldehyde and ethylene oxide upon the phenomena, especially in view of Lenher's recent conclusion (which we think erroneous) about the latter being the primary oxidation product. For while 1% of acetaldehyde nearly wiped out the " induction " without much affecting the " reaction " period, the same amount of ethylene oxide hardly affected the former but greatly lengthened the latter, an observation which was confirmed in another series of experiments made under similar conditions. It should, however, be added that in such experiments it is essential to avoid using a reaction vessel whose inner surface has been recently exposed to aldehyde vapours, for otherwise the results may be misleading. It will be seen that 1% of formaldehyde shortened the " induction " without appreciably affecting the " reaction " period. Further data are given in Tables V and VII and fig. 3 (*q.v.*).

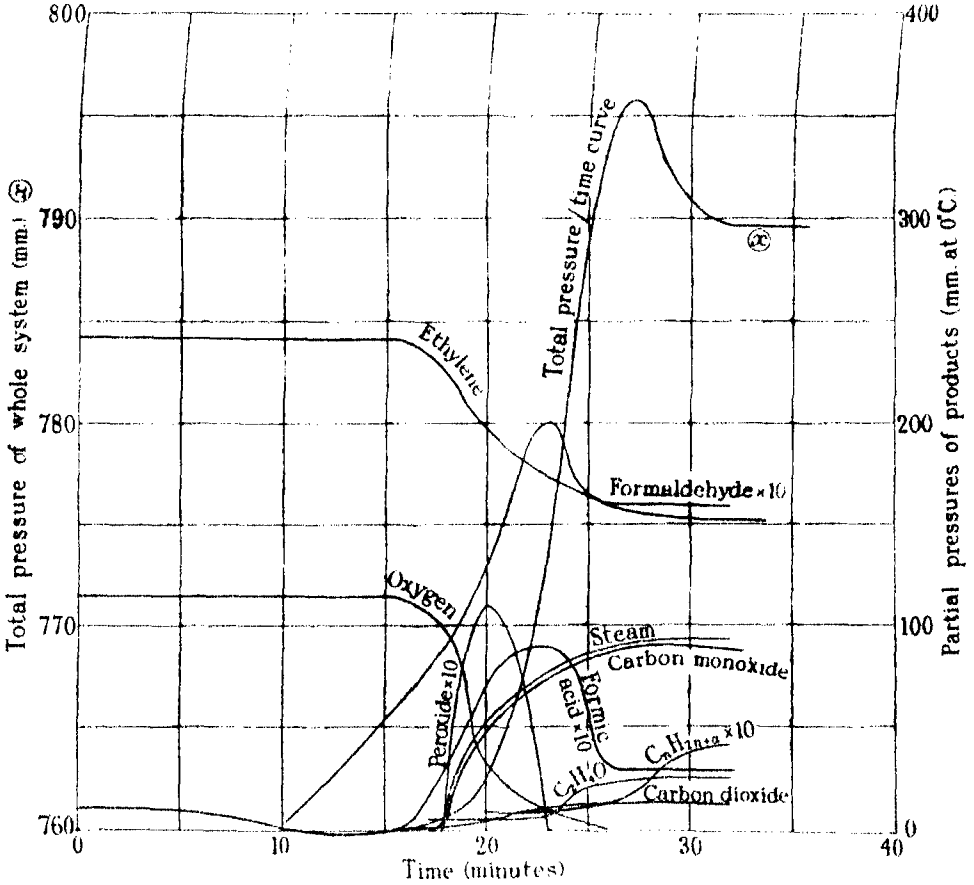


FIG. 2.—Course of the oxidation of a moist $2C_2H_4 + O_2$ medium at 300° C.

Detailed Analyses of the Reaction.

The detailed results of our experiments, divided into four groups according to the particular objects aimed at, are set forth in Tables III, IV, V, VI and VII inclusive, and the accompanying pressure-time curves, figs. 1, 2 and 3. In the tables are given (1) durations (in minutes) of " induction " and " reaction " periods; (2) the observed initial and final pressures (in millimetres) of the dry gaseous medium at the reaction temperature (300° C.); (3) the partial pres-

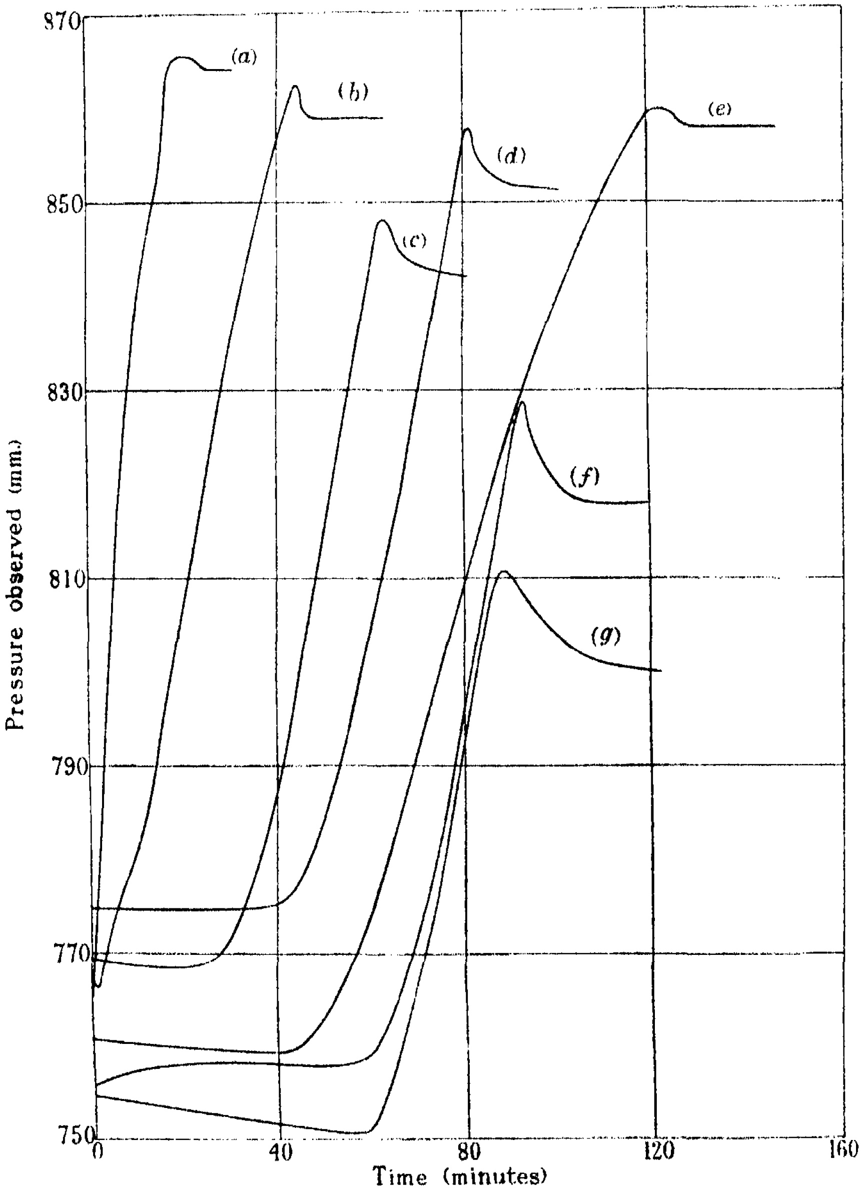
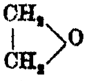


Fig. 3.—Influence of third bodies on reduction and reaction periods of $C_2H_4 + O_2$ medium at 300° C. (*a*) + 1% NO (17); (*b*) + 1% $CH_3.CHO$ (19); (*c*) + 1% $H.CHO$ (18); (*d*) +2% H_2O (15); (*e*)+1%  $\begin{array}{l} CH_2 \\ \vert \\ CH_2 \end{array}\!\!>O$ (20); (*f*) dry (11); (*g*) + 1% H_2O (13). The numbers in brackets correspond to the numbers in the tables. No. 11 is the control experiment for a dry $C_2H_4 + O_2$ medium without any third body.

sures (millimetres) reduced to 0° C. (*a*) of the original ethylene and oxygen, (*b*) of the various *gaseous* constituents of the final system (*i.e.*, CO_2 and CO *plus* residual C_2H_4 and O_2), (*c*) of formaldehyde, formic acid and peroxide (if any) vapour in the final system; and (4) the carbon-hydrogen-oxygen balances of each experiment, the partial pressures of C_2H_4O and H_2O deduced therefrom, and the H_2/O_2 ratio for the so-deduced H_2O, as an index of the general validity of the underlying assumption.

It will be seen that in four experiments out of nineteen this last-named ratio came out between 1·97 and 2·08; in five others it was between 2·1 and 2·25, while in two experiments only did it exceed 2·5. And, seeing that these ratios had to bear the brunt of all errors in the complex analytical work involved, in most cases their deviations from the theoretical 2·0 are no greater than might have been expected. In what follows they will be referred to as "the residual H_2/O_2 ratios."

1st Group.—*Effects of Variations in the Original Mixture Composition* (*Table* III *and fig.* 1).

Five different moist mixtures (H_2O originally present = 8 to 13 mm.) of compositions varying between $5C_2H_4 + O_2$ and $C_2H_4 + 2O_2$ were allowed to react at 300° and atmospheric pressure until nearly all the original oxygen had disappeared. It will be seen that the $2C_2H_4 + O_2$ mixture proved the most reactive of all, and that with all those originally containing more ethylene than the equimolecular proportion an initial pressure rise was sooner or later succeeded by a pressure-fall, the former being more and the latter less pronounced with increasing original oxygen content, as already explained. With the $3C_2H_4 + O_2$ and $2C_2H_4 + O_2$ media a slight pressure-fall was also observed during the "induction period"; but with the $C_2H_4 + O_2$ and $C_2H_4 + 2O_2$ media no pressure fall at all occurred throughout the experiment.

The maximum survivals of C_2H_4O and formaldehyde in the final products were found in the $3C_2H_4 + O_2$ and $2C_2H_4 + O_2$ experiments, while that of formic acid was found in the $C_2H_4 + O_2$ experiment. No peroxide was found except a trace only among the $C_2H_4 + 2O_2$ products. Steam and oxides of carbon were abundantly formed in all cases, the "residual" H_2/O_2 ratios varying between 2·14 and 2·71.

2nd Group.—*Progressive Reaction in a Moist* $2C_2H_4 + O_2$ *Medium.*

In some respects this was the most interesting of the four groups of experiments since its objective was to obtain complete analytical data covering the whole course of reaction of a moist $2C_2H_4 + O_2$ medium. Accordingly in five

Table III.—Effects of Variations in Original Mixture Composition (moisture originally present = 10 to 13 mm.). T = 300° C.

Experiment number	1			2			3			4			5		
Mixture composition	$5C_2H_4 + O_2$.			$3C_2H_4 + O_2$.			$2C_2H_4 + O_2$.			$C_2H_4 + O_2$.			$C_2H_4 + 2O_2$.		
Duration (minutes) of—															
Induction	24			25			16			44			47		
Reaction: Pressure rise	7	20		11	20		11	16		36	36		330+	330+	
Reaction: Pressure fall	13			9			5			0			0		
*Initial pressure (mm.) of dry mixture at 300° C.	750·0			748·8			751·5			754·5			750·0		
*Final pressure of products (mm.) at 300° C.	736·8			749·0			769·0			845·5			881·0		
Partial pressures (mm.) in original mixture at 0° C.—															
C_2H_4	290			263·5			240			178			114·4		
O_2	62			91			114			172			237·2		
†Partial pressures (mm.) of measured products at 0° C.—															
C_2H_4	235·0			185·0			153·0			72·3			6·8		
O_2	2·7			2·7			0·0			1·9			14·3		
CO_2	2·9			10·3			13·6			23·3			45·9		
CO	38·7			60·6			79·0			130·0			153·0		
‡C_nH_{2n+2}	2·9			4·6			4·3			2·6			0·7		
$H_2 : C : O$	14·0			16·5			16·0			14·0			4·6		
H . COOH	3·8			1·2			3·0			12·0			3·5		
Peroxide	Nil			Nil			Nil			Nil			0·1		
Ratio O_2/C_2H_4 used	1·09			1·10			1·31			1·63			2·08		
Ratio CO/CO_2 formed	13·3			5·8			5·8			5·6			4·1		
C-H_2-O_2 balances—	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.
Units in original mixture	580	580	63	527	527	91	480	480	114	356	356	172	229	229	237
Units in measured products	539	500	36	474	407	53	426	338	64	330	178	109	222	23	142
Differences	41	80	27	53	120	38	54	142	50	26	178	63	7	206	95
Calculated as C_2H_4O	41	41	10	53	53	13	54	54	13	26	26	6	7	7	2
Leaving as H_2O	—	39	17	—	67	25	—	88	37	—	152	56	—	199	93
Ratio of residual H_2/O_2	2·29			2·68			2·38			2·71			2·14		

* Excluding any H_2O originally present in the medium, but for products including any H_2O formed during the reaction.

† *I.e.*, all calculated as gaseous at 0° C.

‡ C_nH_{2n+2} = mixture of ethane and propane.

different experiments reaction was suddenly stopped at various selected points during its course and the composition of the medium at each one of them completely ascertained.

The results are detailed in Table IV, and shown graphically in fig. 2, where the partial pressures of each constituent, as well as the total pressure of the whole system, at the reaction temperature (300°) are plotted against time (minutes). It should, however, be noted that whereas those of ethylene, C_2H_4O isomers, steam, oxygen and oxides of carbon are plotted in millimetres as found, those of formaldehyde, formic acid, C_nH_{2n+2} and peroxide have all been multiplied by 10 in order to make them more easily read.

The chief points that emerge are (i) the constant presence of the C_2H_4O isomers and their rapid accumulation as the oxygen in the system approached exhaustion—which strongly indicates C_2H_4O as the primary oxidation-product; (ii) that formaldehyde and formic acid both reached a maximum in the system some time before the pressure rise had ended, and there afterwards rapidly fell off; (iii) that peroxide formation followed upon a certain accumulation of formaldehyde in the system, reached a maximum slightly before the latter, and completely vanished before all the oxygen had disappeared, circumstances which, while difficult to reconcile with any notion of its being a primary oxidation product, point to its having arisen secondarily by peroxidation of aldehyde vapours; and (iv) that steam and oxides of carbon all steadily accumulated in the system throughout the whole reaction period, and especially so as formaldehyde and formic acid were falling off, pointing to these being later oxidation products. Towards the end of the reaction, however, there was a resultant small pressure fall, consistent with the accumulating primary C_2H_4O and a slackening in the production of steam and oxide of carbon. At no period did any free hydrogen appear in the system. The residual H_2/O_2 ratios varied between 2·19 and 2·46; and the data as a whole strongly support the hydroxylation theory.

3rd Group.—Influence of Water Vapour upon the Oxidation.

In this group of experiments (Table V) endeavours were made to ascertain the influence of moisture upon the induction and reaction period, respectively, of a $C_2H_4 + O_2$ medium at 300°, but it proved to be surprisingly small compared with the marked acceleration previously observed in similar experiments with either $2CH_4 + O_2$ (at 447°) or $C_2H_6 + O_2$ (at 316°) media, respectively.*

* Bone and Allum, 'Proc. Roy. Soc.,' A, vol. 134, pp. 585–6 (1932), and Bone and Hill, *ibid.*, A, vol. 129, pp. 443–5 (1930).

Table IV.—Progressive Reaction of a (moist) $2C_2H_4 + O_2$ Mixture (moisture originally present = 8–9 mm.). T = 300° C.

Experiment number	6			7			8			9			10		
Duration (minutes) of— Induction	15			20			16			18			16		
Reaction: Pressure rise	2	2		4	4		7	7		10	10		11	16	
Reaction: Pressure fall	—			—			—			—			5		
*Initial pressure (mm.) of dry mixture at 300° C.	753·4			753·5			752·3			751·0			751·5		
*Final pressure of products (mm.) at 300° C.	753·2			765·0			785·0			781·0			769·0		
Partial pressures (mm.) in original mixture at 0° C.—															
C_2H_4	240·5			240·5			240·5			240·0			240·0		
O_2	114			114			114			114			114		
†Partial pressures (mm.) of measured products at 0° C.—															
C_2H_4	224·0			183·0			179·0			159·5			153·0		
O_2	98·1			33·0			9·8			0·5			0·0		
CO_2	1·3			3·9			10·9			13·3			13·6		
CO	6·4			50·2			69·1			79·3			79·0		
‡C_nH_{2n+2}	Nil			0·8			0·8			1·3			4·3		
$H_2:C:O$	9·0			13·0			20·0			16·0			16·0		
H . COOH	3·0			7·1			9·0			3·0			3·0		
Peroxide	0·6			11·0			0·6			Nil			Nil		
Ratio O_2/C_2H_4 used	1·0			1·42			1·71			1·42			1·31		
Ratio CO/CO_2 formed	4·9			12·9			6·3			5·9			5·8		
$C\text{-}H_2\text{-}O_2$ balances—	C.	H_2.	O_2.	C.	H_2.	O_2	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.
Units in original mixture	481	481	114	481	481	114	481	481	114	480	480	114	480	480	114
Units in measured products	469	461	111	465	411	87	469	390	75	433	342	65	426	338	64
Differences	12	20	3	16	70	27	12	91	39	47	138	49	54	142	50
Calculated as C_2H_4O	12	12	3	16	16	4	12	12	3	47	47	12	54	54	13
Leaving as H_2O	—	Nil	Nil	—	54	23	—	79	36	—	91	37	—	88	37
Ratio of residual H_2/O_2	—			2·34			2·19			2·46			2·38		

* Excluding any H_2O originally present in the medium, but for products including any H_2O formed in reaction.

† *I.e.*, all calculated as gaseous at 0° C.

‡ C_nH_{2n+2} = mixture of ethane and propane.

Table V.—Effect of Moisture on Reaction of a $C_2H_4 + O_2$ Mixture at 300° C.

Experiment number	11	12	13	14	15	16
H_2O content	Nil	Nil	1%	1%	2%	2%
Duration (minutes) of—						
Induction	54	54	60	56	41	48
Reaction: Pressure rise	37 } 50	36 } 52	29 } 54	29 } 50	39 } 50	39 } 55
Reaction: Pressure fall	13	16	25	21	11	16
*Initial pressure (mm.) of dry mixture at 300° C.	755·8	760·8	747·8	768·0	760·5	751·5
*Final pressures (mm.) of products at 300° C.	818·8	814·7	793·0	811·4	836·8	836·0
Partial pressures (mm.) in original mixture at 0° C.						
C_2H_4	178·2	179·9	176·2	181·0	180·4	176·5
O_2	175·3	176·9	173·2	178·0	178·4	177·0
†Partial pressures (mm.) of measured products at 0° C.—						
C_2H_4	73·1	69·5	67·5	75·5	68·6	64·8
O_2	1·7	1·4	0·2	Nil	2·6	1·7
CO_2	18·4	17·8	17·9	17·8	20·6	23·4
CO	132·0	133·0	137·0	141·2	136·0	135·6
‡C_nH_{2n+2}	9·7	13·0	15·2	15·4	6·7	4·2
$H_2:C:O$	13·3	11·0	11·6	11·6	10·0	10·1
H.COOH	10·7	9·3	11·0	11·6	7·0	5·8
Peroxide	Nil	Nil	Nil	Nil	Nil	Nil
Ratio O_2/C_2H_4 used	1·65	1·59	1·59	1·69	1·57	1·57
Ratio CO/CO_2 formed	7·2	7·5	7·7	7·9	6·6	5·8
C-H_2-O_2 balances—	C. H_2. O_2.	C. H_2. O_2.	C. H_2. O_2.	C. H_2. O_2	C. H_2. O_2.	C. H_2. O_2.
Units in original mixture	356 356 175	360 360 177	352 352 173	362 362 178	361 361 178	353 353 177
Units in measured products	340 199 103	336 198 101	343 203 103	364 220 106	323 174 103	313 158 104
Differences	16 157 72	24 162 76	9 149 70	— 142 72	38 187 75	40 195 73
Calculated as C_2H_2O	16 16 4	24 24 6	9 9 2	— — —	38 38 9	40 40 10
Leaving as H_2O	— 141 68	— 138 70	— 140 68	— 142 72	— 149 66	— 155 63
Ratio of residual H_2/O_2	2·08	1·97	2·06	1·97	2·25	2·44

* Excluding any H_2O originally present in the medium, but for products including any H_2O formed during the reaction.

† *I.e.*, all calculated as gaseous at 0° C.

‡ C_nH_{2n+2} = mixture of ethane and propane.

Following upon two control experiments (Nos. 11 and 12) in which the $C_2H_4 + O_2$ medium, previously well dried by passage through a metre long column of specially purified phosphoric anhydride, was admitted into the carefully dried out reaction vessel at 300°, the effects were studied of adding 1% (Nos. 13 and 14) and 2% (Nos. 15 and 16), respectively, of moisture to the similarly dried medium just as it entered the reaction vessel. In each experiment reaction was allowed to proceed until nearly the whole of the original oxygen present had disappeared, and observations were made, not only of the durations of induction and reaction periods, respectively, but also of the initial rise and subsequent fall in pressure during the reaction period.

From the tabulated results it will be seen, however, how little in any respect were the results affected by the initial presence or absence of moisture. Moreover, these observations are in keeping with the result of experiments made many years ago by Andrew and one of us in which it was shown that a 12-weeks P_2O_5-drying of a $C_2H_4 + O_2$ mixture did not in the least diminish its reactivity in a closed tube at 430°–450°, as well as with those of some (as yet unpublished) experiments recently made in our laboratories in which it has been shown that flame-propagation in a $C_2H_4 + O_2$ explosion is undoubtedly accelerated by a similar intensive drying. Hence it may be concluded that the presence of water vapour is not essential to either the slow or the explosive combustion of ethylene.

At the same time, the contrast between the influence of moisture upon the reactivation of $C_2H_4 + O_2$ and $C_2H_6 + O_2$ media, respectively, at 300° and 316°, respectively, and atmospheric pressure in quartz reaction vessels of identically the same dimensions and internal capacities, is very remarkable, as the figures given in Table VI indicate.

Table VI.

Medium.	Duration (minutes) of		
	Induction.	Reaction.	Temperature °C.
(1) $C_2H_4 + O_2$ *dry*	54	50–52	300
(1) $C_2H_4 + O_2$ + 1% H_2O	56–60	50	
(2) $C_2H_6 + O_2$ *dry*	30	70	316
(2) $C_2H_6 + O_2$ + 1% H_2O	10	25	

Attention may also be directed to (i) the complete absence of any peroxide from the end products in all these experiments, although they always contained fair proportions of both formaldehyde and formic acid, as well as (with one exception) of the primary product C_2H_4O, and (ii) to the fact that in four out of the six experiments the residual H_2/O_2 ratio was practically 2·0.

4th Group.—Influence of other Third Bodies upon the Oxidation.

In this final group of experiments (Table VII) the influence of 1% of nitric oxide, formaldehyde, acetaldehyde and ethylene oxide vapour, respectively, upon the reactions of a $C_2H_4 + O_2$ medium (*vide* "control" experiments Nos. 11 and 12 in the previous group) at 300° and atmospheric pressure were studied and the following established :—

(1) *Nitric Oxide* (No. 17) entirely wiped out the induction and greatly shortened the reaction period, without otherwise much influencing the course of events.

(2) *Formaldehyde* (No. 18) about halved the duration of induction without much affecting that of reaction or the general course of events.

(3) *Acetaldehyde* (No. 19) practically eliminated the induction without affecting much the subsequent reaction period.

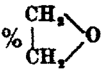
(4) *Ethylene Oxide* (No. 20).—Considerably lengthened the reaction without much affecting the induction period.

The results as a whole indicate that whereas additions of 1% of either moisture of formaldehyde scarcely affected the course of reaction in regard either to the O_2/C_2H_4 ratio used or to the CO/CO_2 ratio in the end products, similar additions of either nitric oxide or C_2H_4O (whether as acetaldehyde or ethylene oxide vapour) tended to increase the former and diminish the latter ratio as though promoting the oxidation of formic to carbonic acid during the penultimate oxidation stage.

Special Experiment on the Oxidation of Ethylene Oxide.

The last named result caused us to make another experiment in which the vacuum reaction vessel at 300° was filled up to 760 mm. with a dry equimolecular mixture of ethylene oxide and oxygen. Almost immediately afterwards the pressure began to rise, and continued to do so during the next 150 minutes. The reaction was then much slower than that observed with an equimolecular $C_2H_4 + O_2$ mixture, and the curve showing the pressure rise,

Table VII.—Effects of other Third Substances upon Reaction of the $C_2H_4 + O_2$ Mixture at 300° C.

Experiment number	17			18			19			20		
Third substance	1% NO			1% $H_2:C:O$			1% $CH_3.CHO$			1% 		
Duration (minutes) of— Induction	0			25			2 (?)			45		
Reaction {Pressure rise	20 } 28			38 } 51			42 } 50			78 } 85		
Reaction {Pressure fall	8			13			8			7		
*Initial pressure (mm.) of dry mixture at 300° C.	758·3			754·1			760·0			759·8		
*Final pressure (mm.) of products at 300° C.	857·2			826·7			849·8			856·0		
Partial pressures (mm.) in original mixture at 0° C.— C_2H_4	358·2			179·0			180·0			177·0		
O_2	241·5			177·0			178·9			177·0		
†Partial pressures (mm.) of measured products at 0° C.— C_2H_4	80·6			64·5			73·2			73·0		
O_2	1·7			0·7			1·2			1·5		
CO_2	19·8			18·8			29·2			27·7		
CO	136·3			138·0			132·0			136·0		
‡C_nH_{2n+2}	3·0			8·9			3·0			1·2		
$H_2:C:O$	14·5			11·3			8·9			10·0		
H.COOH	5·8			11·0			1·7			1·7		
Peroxide	Nil			Nil			Nil			Nil		
Ratio O_2/C_2H_4 used	1·78			1·54			1·66			1·70		
Ratio CO/CO_2 formed	6·9			7·4			4·5			4·9		
C-H_2-O_2 balances—	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.
Units in original mixture	360	360	178	358	358	177	360	360	179	354	354	177
Units in measured products	344	191	103	318	170	101	324	166	103	324	161	104
*Differences	16	169	75	40	188	76	36	194	76	30	193	73
Calculated as C_2H_4O	16	16	4	40	40	10	36	36	9	30	30	8
Leaving as H_2O	—	153	71	—	148	66	—	158	67	—	163	65
Ratio of residual H_2/O_2	2·16			2·24			2·36			2·47		

* Excluding any foreign substance originally present in the medium, but for products including any H_2O formed during the reaction.

† *I.e.*, all calculated as gaseous at 0° C.

‡ C_nH_{2n+2} = mixture of ethane and propane.

fig. 4, was smooth and of a logarithmic type throughout, without any sign of a pressure-fall at the end, in which respect it was in striking contrast with the corresponding curve for the $C_2H_4 + O_2$ reaction. The principal constituents of the cooled medium at the end of the experiment were acetaldehyde, formaldehyde, formic acid, oxides of carbon and steam, with a little hydrogen and ethane, the percentage composition of the nitrogen-free gaseous products at the end of reaction being as follows :—

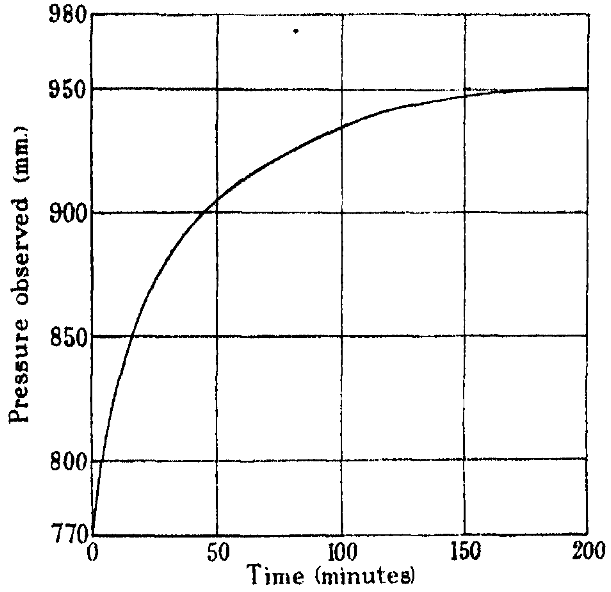


FIG. 4.—Reaction of a $\begin{matrix}CH_2\diagdown\\ |\quad\;\; O\\ CH_2\diagup\end{matrix}$ + O_2 mixture at 300° C.

$$CO_2 = 32{\cdot}5,\ CO = 64{\cdot}5,\ H_2 = 1{\cdot}5,\ C_2H_6 = 0{\cdot}1,\ O_2 = 1{\cdot}4\%.$$

It may also be noted that the ratio CO/CO_2 in the products was practically 2·0 or very much lower than in the products of any of the ethylene oxidation experiments.

Conclusions.

(1) The reaction between ethylene and oxygen at 300° and atmospheric pressure is substantially homogeneous and is preceded by a well-marked induction period during which a small amount of aldehyde (but no peroxide) appears. This induction period is practically eliminated by a previous addition of 1% of either nitric oxide or acetaldehyde, while a similar addition of formal-

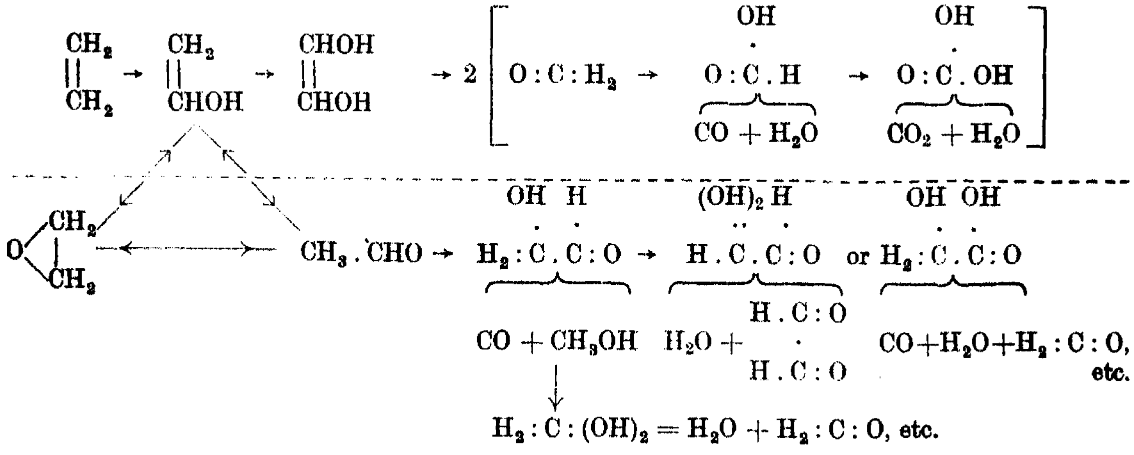
dehyde vapour shortens it. The subsequent reaction is accelerated by previous similar additions of nitric oxide or acetaldehyde but retarded by ethylene oxide.

(2) The reaction does not depend upon the presence of water vapour, neither the induction nor the reaction periods being materially affected thereby.

(3) The most reactive of all ethylene-oxygen media is $2C_2H_4 + O_2$, and C_2H_4O is the initial oxidation product.

(4) The initial stage of oxidation certainly does not involve any "peroxidation" but, on the contrary, an "hydroxylation" of the ethylene to vinyl alcohol $H_2C:CHOH$, any accumulation of which in the medium is rapidly transformed into an equilibrium mixture of the three C_2H_4O-isomers in proportions dependent upon temperature and pressure. In the present experiments (*i.e.*, at 300° and atmospheric pressure) such equilibrium ratio was approximately 4 vinyl alcohol : 10 ethylene oxide : 1 acetaldehyde; but other experiments now proceeding on the pressure-oxidation of ethylene have shown that increasing pressure shifts the equilibrium so rapidly over to acetaldehyde as almost to obliterate the ethylene oxide. This circumstance possibly accounts for the confusion between previous workers as regards which of the three C_2H_4O-isomers is initially formed; in our view it is undoubtedly vinyl alcohol.

(5) All the available evidence now points to the normal course of oxidation being essentially a series of successive "hydroxylations" as follows, the uppermost representing the usual and main routes at atmospheric pressure, and those below occasional and alternative ones:—



CH₂ ‖ CH₂ → CH₂ ‖ CHOH → CHOH ‖ CHOH → 2 [O : C : H₂ → O : C . H (OH) → O : C . OH (OH)]
CO + H₂O
CO₂ + H₂O
O(CH₂)₂
CH₃ . CHO → H₂ : C . C : O (OH H) → H . C . C : O ((OH)₂ H) or H₂ : C . C : O (OH OH)
CO + CH₃OH
H₂O + H . C : O . H . C : O
CO+H₂O+H₂ : C : O, etc.
H₂ : C : (OH)₂ = H₂O + H₂ : C : O, etc.

Such scheme, it may be observed, would account for the formation of glyoxal as a side-product, as well as the finding of methyl alcohol by Pichler and Reder among the pressure-oxidation products of ethylene.

In conclusion, we desire to thank the Gas Light & Coke Company for their Research Fellowship enabling one of us (A. E. H.) and the Department of Scientific and Industrial Research for a grant enabling another of us (H. F. R.) to devote their whole time to the research.

Summary.

Investigation of the reaction at 300° and atmospheric pressure of various ethylene-oxygen mixtures of compositions ranging between $5C_2H_4 + O_2$ and $C_2H_4 + 2O_2$ has shown that:—

(1) Under such conditions the reaction is substantially homogeneous and is preceded by a well-marked induction period during which a small amount of aldehyde (but no peroxide) appears. This induction period is practically eliminated by a previous addition of 1% of either nitric oxide or acetaldehyde, while a similar addition of formaldehyde vapour shortens it. The subsequent reaction is accelerated by previous additions of nitric oxide or acetaldehyde but retarded by ethylene oxide.

(2) The reaction does not depend upon the presence of water vapour, neither the induction nor the reaction periods being materially affected thereby.

(3) The most reactive of all ethylene-oxygen media is $2C_2H_4 + O_2$, and C_2H_4O is the initial oxidation product.

(4) The initial stage of oxidation certainly does not involve any "peroxidation" but, on the contrary, an "hydroxylation" of the ethylene to vinyl alcohol $H_2C:CHOH$, any accumulation of which in the medium is rapidly transformed into an equilibrium mixture of the three C_2H_4O-isomers in proportions dependent upon temperature and pressure. In the present experiments (*i.e.*, at 300° and atmospheric pressure) such equilibrium ratio was approximately 4 vinyl alcohol : 10 ethylene oxide : 1 acetaldehyde; but other experiments, now proceeding, on the pressure-oxidation of ethylene have shown that increasing pressure shifts the equilibrium so rapidly over to acetaldehyde as almost to obliterate the ethylene oxide.

(5) The normal course of oxidation is throughout essentially a series of successive hydroxylations.

Antimonial Analogues of the Acridine Series. Dihydrostibacridines.

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(Received August 2, 1933.)

In pursuing our investigation on the antimony analogues of certain nitrogen ring-systems, we have now succeeded in obtaining derivatives of dihydrostibacridine, of which some of the corresponding arsenic compounds have been studied recently by Gump and Stolzenburg.*

The starting material for this work was *o*-aminodiphenylmethane obtained from the corresponding nitro derivative which, in turn, was prepared from *o*-nitrobenzyl chloride and benzene by Tanesescu's† modification of the Friedel-Crafts reaction.

The introduction of antimony was effected by the Bart-Schmidt process, the yield of *diphenylmethane-2-stibonic acid* (VI) not, however, being very good. Reduction of this acid with sulphur dioxide in the presence of hydrochloric acid gave *diphenylmethane-2-stibine dichloride* (VII).

In the carbazole series discussed previously‡ ring closure could be effected, either by heating the stibonic acid with concentrated sulphuric acid, or by refluxing the stibine dichloride *in vacuo.* In the present series the closing of the ring was not so easy. Heating the above dichloride under 20 mm. pressure did not lead to the elimination of hydrogen chloride, indeed, the substance was comparatively stable although antimony chloride was slowly formed. Furthermore, when the stibonic acid was heated with concentrated sulphuric acid considerable decomposition took place and, probably, some sulphonation. Ring closure was ultimately effected by heating the diphenylmethane-2-stibonic acid with a considerable quantity of acetic anhydride containing a little sulphuric acid. From the *stibacridinic acid* (V) so produced, 10-*chloro*-9 : 10-*dihydrostibacridine* (III) was obtained in the usual manner. Treatment of this substance with alkalis produced the corresponding *oxide* (I) from which the 10-*bromo*- and 10-*iodo*-9 : 10-*dihydrostibacridines* (III) were made. This iodide was also obtained by double decomposition of the chloride with sodium iodide in acetone.

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* 'J. Amer. Chem. Soc.,' vol. 53, p. 1428 (1931).

† 'Bull. Soc. chim.,' vol. 39, p. 1453 (1926).

‡ 'Proc. Roy. Soc.,' A, vol. 127, p. 1 (1930).

Replacement of the halogen by alkyl or aryl groups may be effected by means of the Grignard reagent and in this way there was obtained 10-*methyl*-9 : 10-*dihydrostibacridine* (IV). This substance did not combine with methyl iodide but did decolourize bromine and iodine in chloroform. The resulting dibromide and di-iodide could not, however, be isolated for they evolved the corresponding methyl halide during purification. The Grignard reaction did not proceed very smoothly when phenyl magnesium bromide was used; considerable purification of the product was necessary and this was further complicated by oxidation of the antimonial. Ultimately the crude product was treated with hydrochloric acid and chlorine and 10-*phenyl*-9 : 10-*dihydrostibacridine dichloride* (II) thus obtained.

In common with other antimonials, the primary series, as exemplified by diphenylmethane-2-stibine dichloride (VII), is easily converted into the secondary series by the action of warm alkalis. *Tetrakis*-2-*diphenylmethanedistibine oxide* (IX) was thus produced and reacted with the halogen acids to give the respective *halides* (VIII). *Bis*-2-*diphenylmethanestibine chloride* added on chlorine to form the *trichloride* (X) which slowly liberated hydrogen chloride when heated under reduced pressure producing 10-2′-*diphenylmethane*-9 : 10-*dihydrostibacridine dichloride* (XI). Considerable difficulty was experienced in separating this compound from unchanged trichloride. The oxygen derivatives, obtained by treating the crude mixture of chlorides with alkali, were more easily separated for 10-2′-*diphenylmethane*-9 : 10-*dihydrostibacridine oxide* (XII) was found to be more soluble in acetone than the *bis*-2-*diphenylmethanestibinic acid*.

Experimental.

Diphenylmethane-2-*stibonic acid* (VI).—*o*-aminodiphenylmethane hydrochloride (22 gm.) in 250 c.c. of water and 44 c.c. of 5 N-hydrochloric acid were diazotized with sodium nitrite (7 gm.) in 30 c.c. of water. To the diazo solution was added a solution of 14·5 gm. of antimony oxide in 45 c.c. of hydrochloric acid ($d = 1 \cdot 16$) and 60 c.c. of glycerine. To the ice-cooled mixture there was added, with good stirring, 5 N-sodium hydroxide until just alkaline to litmus, and this alkalinity was maintained by further small additions of alkali from time to time. When the froth had subsided a further 10 c.c. of sodium hydroxide were added (making about 150 c.c. in all) and stirring was continued until an azo colour with H. acid (8-amino-1-hydroxynaphthalene-3 : 6-disulphonic acid) was no longer obtained. The mixture was gently warmed for some 15 minutes and then filtered. The filtrate was nearly neutralized with

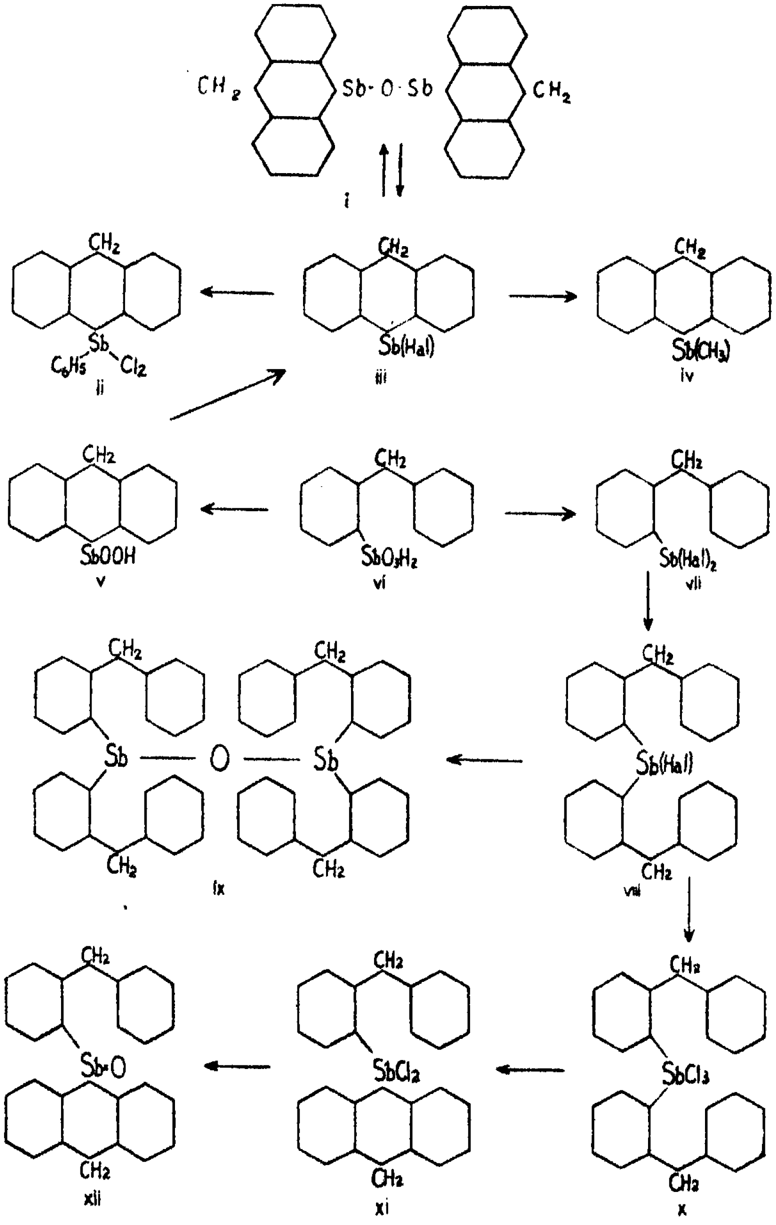

CH2
Sb·O·Sb
CH2
i
CH2
Sb
C6H5
Cl2
ii
CH2
Sb(Hal)
iii
CH2
Sb(CH3)
iv
CH2
SbOOH
v
CH2
SbO3H2
vi
CH2
Sb(Hal)2
vii
CH2
Sb
O
Sb
CH2
CH2
CH2
ix
CH2
Sb(Hal)
CH2
viii
CH2
Sb·O
CH2
xii
CH2
SbCl2
CH2
xi
CH2
SbCl3
CH2
x

Fig. 1.

dilute hydrochloric acid (until faintly alkaline to turmeric paper) and saturated with carbon dioxide. Colouring matter and inorganic antimony oxide were filtered off and the stibonic acid precipitated with hydrochloric acid. The product was finally obtained as a colourless amorphous powder.

The inorganic antimony oxide, separated as above, carries down with it some of the stibonic acid, but this may be recovered by treating the by-product with warm 5 N-hydrochloric acid, extracting the residue with hot dilute sodium hydroxide and acidifying the alkaline solution.

Diphenylmethane-2-stibonic acid was easily soluble in chloroform and methylene dichloride and in mixtures of these solvents with the alcohols, acetone or benzene. It was less soluble in benzene and hot alcohol. By very slow crystallization from a mixture of methylene dichloride and alcohol it could be obtained in small pale coloured needles. This acid is only slowly soluble in hot dilute sodium hydroxide.

Found.—Sb = 37·7 ; 37·4%. $(C_6H_5 . CH_2 . C_6H_4SbO)_3 O_2 (OH)_2$ requires Sb = 37·3%.

Diphenylmethane-2-stibine dichloride (VII).—Diphenylmethane-2-stibonic acid (2 gm.) was triturated with about 20 c.c. of concentrated hydrochloric acid and 5 c.c. of methyl alcohol. The mixture was then reduced with sulphur dioxide and a trace of potassium iodide and left for half an hour. A little more acid was added to ensure precipitation of any dissolved dichloride and the dirty white crystalline precipitate was then recrystallized from a mixture of carbon disulphide and petroleum (b.p. 60°–80° C.). Several recrystallizations were necessary before the product was obtained pure in long, colourless needles, m.p. 129°–130° C. easily soluble in the usual organic solvents with the exception of petroleum.

Found.—C = 43·5 ; H = 3·1 ; Cl = 19·6 ; Sb = 33·8% = 100·0%. $C_{13}H_{11}Cl_2Sb$ requires C = 43·4 ; H = 3·1 ; Cl = 19·7 ; Sb = 33·8%.

Diphenylmethane-2-stibine di-iodide (VII).—The above dichloride (1·2 gm.) in acetone was treated with a solution of sodium iodide (0·5 gm.) in the same solvent. Sodium chloride was removed and the filtrate evaporated. The residue recrystallized from a mixture of carbon disulphide and petroleum (b.p. 40°–60° C.) in beautiful golden yellow prismatic crystals, m.p. 95° C. Its solubilities are similar to those of the dichloride.

Found.—C = 28·6 ; H = 2·1 ; I = 46·3 ; Sb = 22·6%. $C_{13}H_{11}I_2Sb$ requires C = 28·7 ; H = 2·0 ; I = 46·8 ; Sb = 22·4%.

Diphenylmethane-2-stibine dibromide (VII).—A solution of the chloride in acetone or alcohol was poured with stirring into slight excess of ice-cold dilute ammonia. The supernatant liquid was decanted from the somewhat sticky mass of oxide which was quickly washed with water and treated with hydrobromic acid ($d = 1 \cdot 3$). The mixture was then extracted with carbon disulphide and the solvent evaporated. Recrystallized from a mixture of this medium and petroleum, the dibromide yielded colourless plates, m.p. 121° C.

Found.—Sb = 27·4%. $C_{13}H_{11}Br_2Sb$ requires Sb = 27·2%.

Diphenylmethane-2-stibine oxide. $C_6H_5 . CH_2 . C_6H_4 . SbO$.—This oxide obtained as in the preceding preparation, after thorough washing with ice-cold water was extracted with methylene dichloride, the solution evaporated and the residue taken up in acetone. The solution was filtered (with charcoal) and poured into cold water. The oxide separated as a colourless microcrystalline powder, m.p. 82°–83° C. It was fairly stable when pure and dry, but it rapidly shed antimony oxide in contact with dilute alkali. The oxide dissolved readily in chloroform, benzene or acetone, but was less soluble in methyl and ethyl alcohol.

Found.—Sb = 39·6%. $C_{13}H_{11}OSb$ requires Sb = 40·0%.

10-*chloro*-9 : 10-*dihydrostibacridine* (III).—Diphenylmethane-2-stibonic acid (6 gm.) was heated on a steam bath for 3 hours with 40 c.c. of acetic anhydride containing 1·5 c.c. of concentrated sulphuric acid. Most of the stibonic acid dissolved in this mixture, the solution, which was at first pale brown becoming considerably darker towards the end. The mixture was poured into warm water (400 c.c.) when the stibacridinic acid was precipitated as a light brown powder which quickly settled to the bottom. After 1 hour the precipitate was washed with water and dried. When dry it was treated with excess of ice-cold hydrochloric acid whereby it was converted into a pasty mass of the *stibacridine trichloride*. This was filtered to free it from excess of acid and dissolved in the least possible quantity of warm methyl alcohol and the solution again filtered with the aid of charcoal. It was now reduced with sulphur dioxide in the usual way and, on addition of hydrochloric acid, the 10-chloro-9 : 10-dihydrostibacridine was obtained as a dirty brown, sometimes oily, crystalline precipitate. This was taken up in carbon disulphide, and petroleum (b.p. 60°–80° C.) added until a distinct turbidity was obtained when a certain amount of oily by-product slowly separated. The supernatant liquid was decanted and allowed to evaporate when crystals of the chloride were obtained. After several crystallizations the product was obtained in the form of fan-shaped clusters of colourless needles, m.p. 105° C., easily soluble in the usual organic solvents though only slightly soluble in petroleum.

Found.—C = 48·2; H = 3·3; Cl = 11·0; Sb = 37·7%. $C_{13}H_{10}ClSb$ requires C = 48·3; H = 3·1; Cl = 11·0; Sb = 37·7%.

10-*iodo* 9 : 10-*dihydrostibacridine* (III).—Obtained either from the chloride by treatment with sodium iodide in acetone or by the action of hydriodic acid on the oxide. When recrystallized from carbon disulphide and petroleum it formed yellow needles, m.p. 160°–162° C. Its solubility in various solvents is somewhat less than that of the chloride.

Found.—C = 37·4; 37·7; H = 2·4; 2·3; I = 30·3; Sb = 29·2%. $C_{13}H_{10}ISb$ required C = 37·6; H = 2·4; I = 30·6; Sb = 29·4%.

10-*bromo*-9 : 10-*dihydrostibacridine* (III).—Prepared by the action of hydrobromic acid on the oxide, the bromide being extracted with carbon disulphide. Evaporation of the solution gives colourless or slightly yellow acicular plates. If recrystallized very slowly from a mixture of carbon disulphide and petroleum (b.p. 60°–80° C.) it may be obtained in the form of cubes, m.p. 112° C.

Analysis.—Br = 21·8; Sb = 33·0%. $C_{13}H_{10}BrSb$ requires Br = 21·7; Sb = 33·1%.

10 : 10′-*oxy-bis*-9 : 10-*dihydrostibacridine* (I).—This oxide was obtained when any of the foregoing 10-halogeno derivatives in acetone were added to an excess of dilute aqueous ammonia with stirring. A colourless amorphous precipitate was formed and crystallized from a mixture of methylene dichloride and alcohol. Colourless microcrystalline powder which began to soften at 211° C. and sintered at 215° C. Moderately soluble in chloroform, methylene dichloride and acetone; sparingly soluble in alcohol.

Found.—C = 52·5; H = 3·5; Sb = 41·3%. $C_{26}H_{20}OSb_2$ requires C = 52·7; H = 3·4; Sb = 41·2%.

Stibacridinic acid (V).—The stibacridinic acid obtained as an intermediate in the preparation of 10-chloro-9 : 10-dihydrostibacridine was purified by dissolving in a little concentrated hydrochloric acid and acetone. The solution was now poured with stirring into excess of warm $\frac{1}{2}N$-sodium hydroxide, the solution filtered and the acid precipitated with dilute mineral acid. The product was separated, well washed with water and, after drying, was dissolved in chloroform and reprecipitated with methylated spirit. Pale coloured powder.

Found.—Sb = 38·9%. $C_{13}H_{11}O_2Sb$ requires Sb = 38·0%.

10-*methyl*-9 : 10-*dihydrostibacridine* (IV).—A solution of methyl magnesium iodide made from 1·5 c.c. of methyl iodide and 0·36 gm. of magnesium in 25 c.c. of dry ether was added to 4 gm. of 10-iodo-9 : 10-dihydrostibacridine in 125 c.c. of ether (even with this large volume all the iodo-compound was not dissolved). The colour was slowly discharged and the reaction was completed by refluxing for 15 minutes. The ether was distilled off and the residue treated with water whereby a soft yellow mass was obtained. By repeated crystallizations from methylene dichloride containing a little methyl alcohol the 10-methyl derivative separated in colourless spangles which softened at 98° C. and melted at 101° C., easily soluble in most organic solvents.

Found.—C = 55·4 ; H = 4·4 ; Sb = 40·0%. $C_{14}H_{13}Sb$ requires C = 55·5 ; H = 4·3 ; Sb = 40·2%.

10-*methyl*-9 : 10-*dihydrostibacridine dichloride.*—When a solution of 10-methyl-9 : 10-dihydrostibacridine in methylene dichloride was treated with iodine in the same solvent, the halogen solution was decolourized and on evaporation a gummy mass of the di-iodide was obtained. Attempts to purify this product resulted in the loss of methyl iodide and the formation of the 10-iodo derivative, m.p. and mixed m.p. 160°–162° C. ; Sb = 29·7%.

A similar decomposition took place when bromine was used.. The dichloride, however, was sufficiently stable to permit of isolation and was obtained as colourless diamond-shaped plates which melted at 177°–178° C. with evolution of gas.

Found.—Sb = 32·5%. $C_{14}H_{13}Cl_2Sb$ requires Sb = 32·6%.

10-*phenyl*-9 : 10-*dihydrostibacridine dichloride* (II).—The Grignard reaction with phenyl magnesium bromide did not proceed so smoothly as with the methyl derivative and the product when worked up as in the preceding experiment gave only a dark gummy mass. During purification of this substance considerable oxidation was found to have taken place and so the product was treated with hydrochloric acid, extracted with chloroform and chlorine added in the hope that the dichloride would be more easily separated. The chloroform was evaporated off and the residue dissolved in a mixture of acetone and alcohol. On allowing to crystallize slowly the dichloride was obtained as colourless hexagonal crystals with the usual solubilities. It melted at 221°–223° C.

Found.—Sb = 27·8 ; Cl = 15·9%. $C_{19}H_{15}Cl_2Sb$ requires Sb = 27·9 ; Cl = 16·3%.

Tetrakis-2-*diphenylmethanedistibine oxide* (IX).—(1) Diphenylmethane-2-stibine dichloride (3 gm.) in a little acetone was poured into excess of dilute ammonia and the oxide after filtration was suspended in 30 c.c. of acetic acid (about two-thirds dissolved) and 15 c.c. of 20% tartaric acid solution added. After 2 days a colourless crystalline precipitate was formed which was dissolved in a mixture of acetone and methyl alcohol. Ammonia was added until alkaline and then excess of water. The secondary oxide separated and was crystallized from a mixture of methylene dichloride and alcohol. Colourless needles, m.p. 117° C.

(2) A better yield, but a less pure product was obtained by adding the dichloride in acetone to a considerable excess of very dilute ammonia, heating on the steam bath for 2 hours and leaving overnight. The product was filtered off and separated from antimony oxide by extraction with hot acetone. It was purified as above. The oxide was easily soluble in chloroform, methylene dichloride and benzene, somewhat less in acetone and only moderately soluble in hot methyl or ethyl alcohol.

Found.—C = 67·5; 67·2; H = 5·0; 4·7; Sb = 26·4%. $C_{52}H_{44}OSb_2$ requires C = 67·3; H = 4·7; Sb = 26·3%.

Bis-2-diphenylmethanestibine chloride (VIII). $(C_6H_5{-}CH_2{-}C_6H_4)_2Sb\,.\,Cl$.—This chloride was obtained by adding excess of ice-cold concentrated hydrochloric acid to a solution of the above oxide in a little acetone. The crystalline precipitate was recrystallized from methylene dichloride and alcohol. Slow evaporation results in the formation of fine colourless hair-like needles, m.p. 87·5° C., easily soluble in methylene dichloride, acetone and benzene, considerably less soluble in alcohol.

Found.—C = 63·5; H = 4·7; Cl = 7·3; Sb = 25·0%. $C_{26}H_{22}ClSb$ requires C = 63·5; H = 4·5; Cl = 7·2; Sb = 24·8%.

Bis-2-diphenylmethanestibine bromide (VIII).—Prepared in a similar manner to the chloride and possessing like properties and solubilities. Colourless needles, m.p. 86·5° C.

Found.—Sb = 22·8; Br = 15·0%. $C_{26}H_{22}BrSb$ requires Sb = 22·7; Br = 14·9%.

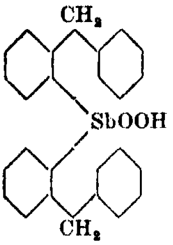
Bis-2-diphenylmethanestibine iodide (VIII).—Formed either by the above method or by the action of sodium iodide on the chloride, was recrystallized from a mixture of carbon disulphide and petroleum (b.p. 60°–80° C.) containing a little alcohol and separated in light yellow clusters of fine needles, m.p. 73°–75° C., sparingly soluble in cold alcohol.

Found.—Sb = 21·0%. $C_{26}H_{22}ISb$ requires Sb = 20·9%.

Bis-2-diphenylmethanestibine trichloride (X).—Obtained by direct addition of chlorine to the monochloride in methylene dichloride, was difficult to obtain crystalline for, like many of these compounds, it persisted in coming down oily. It was finally crystallized by treating a solution in methylene dichloride with methyl alcohol containing a little concentrated hydrochloric acid and then allowing the solvent to evaporate very slowly. Colourless diamond shaped plates, m.p. 129° C. Very soluble in methylene dichloride, benzene and acetone, less so in ether, methyl and ethyl alcohols.

Found.—C = 55·7, 55·4 ; H = 3·9, 4·1 ; Cl = 18·7 ; Sb = 21·8%. $C_{26}H_{22}Cl_3Sb$ requires C = 55·5 ; H = 3·9 ; Cl = 18·9 ; Sb = 21·7%.

Bis-2-diphenylmethanestibinic acid.—When the foregoing trichloride in a little acetone was treated with warm dilute ammonia and then heated on a steam bath for 10 minutes a colourless crust was obtained. This crystallized from a mixture of acetone and chloroform as a colourless powder consisting of small spangles. Moderately soluble in chloroform, acetone and warm acetic acid, but not very soluble in other solvents, m.p. 248° C.



Found.—C = 64·2 ; H = 4·9 ; Sb = 25·3, 25·4%. $C_{26}H_{23}O_2Sb$ requires C = 63·8 ; H = 4·7 ; Sb = 24·9%.

This acid was also obtained by oxidation of the corresponding oxide with hydrogen peroxide.

10-2′-*diphenylmethane*-9 : 10-*dihydrostibacridine dichloride* (XI).—When the preceding trichloride was heated at 150° to 180° C. under 18–20 mm. pressure, hydrogen chloride was slowly evolved and a dark brown oil was obtained. This oil set to a jelly on cooling and consisted mostly of unchanged trichloride together with some dichloride and a little diphenylmethane. It was not found possible to separate the dichloride in a pure state and so the acetone solution of the crude product was treated with slight excess of dilute ammonia. The light brown precipitate was warmed with a mixture of acetone and methyl alcohol when the 10-2′-*diphenylmethane*-9 : 10-*dihydrostibacridine oxide* (XII) and some bis-2-diphenylmethanestibinic acid dissolved. The undissolved stibinic acid was filtered off and the filtrate concentrated in stages, the final crops giving the oxide. By repeating the process the oxide was obtained as a colourless floury powder readily soluble in chloroform, less soluble in acetone and considerably less soluble in ethyl and methyl alcohols. It softened to a clear gum at 158°–160° C.

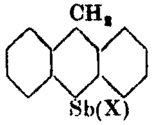
Found.—C = 66·2 ; H = 4·5 ; Sb = 25·9%. $C_{26}H_{21}OSb$ requires C = 66·3 ; H = 4·5 ; Sb = 25·9%.

Treatment of the oxide with hydrochloric acid and recrystallization of the product from a mixture of acetone and methyl alcohol gave the chloride as a slightly coloured microcrystalline powder which was fairly easily soluble in chloroform, benzene, carbon disulphide or acetone ; less soluble in the alcohols. m.p. with darkening 220°–224° C.

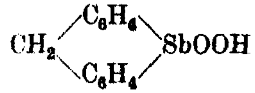
Found.—Sb = 22·4%. $C_{26}H_{21}Cl_2Sb$ requires Sb = 23·2%.

Summary.

Continuing our investigations on cyclic antimonials we have now succeeded in obtaining derivatives of dihydrostibacridine (i).



(i)

The starting-point of this work was *o*-aminodiphenylmethane which was converted by the Bart-Schmidt reaction into *diphenylmethane*-2-*stibonic acid* $C_6H_5 . CH_2 . C_6H_4 . SbO_3H_2$ from which, by reduction in presence of hydrochloric acid, there was obtained *diphenylmethane*-2-*stibine dichloride.* Unlike the corresponding antimony carbazole derivative, the dichloride could not be made to undergo ring closure with loss of hydrogen chloride. The ring was, however, closed when the elements of water were abstracted from the stibonic acid under suitable conditions. The *stibacridinic acid*  $CH_2\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle SbOOH$ so produced was transformed in the usual way into the 10-halogeno-9 : 10-*dihydrostibacridines* ($X = Cl$, Br or I). From the iodide by use of Grignard reagents there was obtained 10-*methyl*-9 : 10-*dihydrostibacridine* and 10-*phenyl*-9 : 10-*dihydrostibacridine dichloride.*

Diphenylmethane-2-stibine dichloride in contact with dilute alkali gave the corresponding *oxide* which rapidly shed half its antimony producing *tetrakis*-2-*diphenylmethanedistibine oxide* $[(C_6H_5 . CH_2 . C_6H_4)_2Sb]_2O$. This oxide when treated with halogen acids formed *bis*-2-*diphenylmethanestibine halides* $(C_6H_5 . CH_2 . C_6H_4)_2Sb . X$. By the addition of chlorine to the chloride there was obtained the *trichloride* which, with difficulty, was made to lose hydrogen chloride giving 10-2′-*diphenylmethane*-9 : 10-*dihydrostibacridine dichloride.* Purification of this compound was not easy but it was finally accomplished through the corresponding *oxide.*

Atomic Constants deduced from Secondary Cathode Ray Measurements.

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(Received August 4, 1933.)

§ 1. It is well known that the accurate measurement of the energies of the secondary cathode rays excited by homogeneous X-rays can yield results capable of supplementing our knowledge of the most probable values of the fundamental atomic constants. This application of the "magnetic spectrograph" has already been discussed by one of us[†] in some detail, and Kretschmar[‡] has published an account of accurate measurements on X-ray electrons, from which he has deduced very consistent values of e/m_0. In this work Kretschmar used molybdenum K radiations, and produced his magnetic fields by a large solenoid.

§ 2. We have during the past fifteen months photographed a large number of secondary cathode-ray spectra, using copper K as primary X radiation. For a few elements, for which the results will be detailed later in this paper, we have made very careful measurements of the energies, cross-checking the observations by working in a wide range of magnetic fields.

The arrangement used was substantially that of earlier experiments,[§] with a number of improvements in detail. As before, a pair of Helmholtz coils, nearly 40 cm. in diameter and giving a field at the centre of about 23 gauss per ampere, has been used to produce the approximately uniform magnetic fields required in these experiments. The coils were wound on a pair of specially cast brass formers, accurately turned and finished.[||] Screw adjustments were provided for accurately setting and rigidly holding the coils in place, and the pair was mounted on a massive bronze base. All materials used were tested for absence of ferromagnetic impurities.

The field at the centre of the coil system (per unit current) was calculated from the dimensions of the coils and their distance apart. As a check on this value, a standardizing solenoid was specially wound on a cylinder of length 100 cm. and diameter 5 cm. This solenoid was carefully aligned along the axis of the Helmholtz coils, the centres of the two systems being set in coincidence, and their common axis horizontal and at right angles to the magnetic meridian. A short magnet, mounted on a galvanometer mirror, was suspended freely at the common centre of the systems. It was thus possible, making adjustments from observations using a lamp and scale, to ensure that the field of the solenoid exactly neutralized that of the Helmholtz coils at the centre. This adjustment made, the currents in the two systems were compared by the usual method, using a potentiometer and standard resistances. The required constant of the Helmholtz system is thus obtained in terms of that of the standardizing solenoid and of the ratio of two currents—a ratio which can easily be measured to a high degree of accuracy. As an additional check the fields of the two Helmholtz coils (which were not quite identical, owing to slight differences in winding) were separately compared with that of the solenoid.

[†] Robinson, 'Phil. Mag.,' vol. 14, p. 605 (1932). Referred to hereinafter as 'R.P.M.'

[‡] 'Phys. Rev.,' vol. 43, p. 417 (1933).

[§] Robinson, 'Proc. Roy. Soc.,' A, vol. 104, p. 455 (1923).

[||] We are especially indebted to Mr. M. Niblett, of the East London College Instrument Shop, who supervised the making of the coils, and suggested and carried out a number of improvements in the method of mounting them.

The two values of the required constant, obtained (i) by direct calculations from dimensions, and (ii) by comparison with the solenoid, agreed to within the estimated accuracy obtainable in either method; the two values were, in fact, $23 \cdot 43_3$ and $23 \cdot 42_8$ respectively.

The variation of the field of the Helmholtz coils with distance from the centre, in the plane normal to the axis, was calculated as in Maxwell, "Electricity and Magnetism," and—mainly as a check on the sensitivity of the magnetometric calibration—was also verified at a few selected distances with the standardizing solenoid. The correction for incomplete homogeneity of field was made by Hartree's[†] method—checked by a less elegant *ad hoc* and partly graphical method. The calculation of the effective values of rH (H gauss = magnetic field, r cm. = radius of curvature of path of an electron in a plane perpendicular to H) was much simpler and almost certainly more accurate than in the earlier published work of Robinson. The most important simplification has been achieved by the use of an X-ray tube with a much reduced cathode-anticathode distance; with this tube, no compensating coils[‡] are required to keep the cathode stream focussed on the anticathode when the magnetic field is applied. When compensating coils were used, the correction for the effect of their stray field was not easy to apply, and its magnitude was almost certainly underestimated in the earlier work.

With the present arrangement, the cathode is initially set slightly off the axis of the tube, in such a way that, in the field of the coils, the cathode stream is roughly focussed on the anticathode; the focussing is completed by rocking the tube slightly, by means of adjusting screws or wedges, about two bearings until the maximum intensity of X-radiation is obtained. This is tested by a barium platinocyanide screen, mounted in the position normally occupied by the target of the element to be examined. In this way, it has been found possible to get a much more efficient source of X-rays than in the earlier experiments, and the lengths of the exposures have been correspondingly reduced. In most cases—depending on the type of target and of photographic plate—exposures of 2 to 3 hours are sufficient, with the tube (a "gas-filled" tube, water- and air-cooled) running at 8–10 milliamperes and 20–50 kilovolts.

[†] 'Proc. Camb. Phil. Soc.,' vol. 21, p. 746 (1923).

[‡] *Cf.* Robinson, *loc. cit.*, p. 460 (1923).

The radii of curvature, r, of the electron paths on which the most important of the measurements were made, lay in general between about 4·5 and 5·5 cm. They were adjusted to fall within this range by appropriate selection of the magnetic field. The camera was, therefore, so placed between the coils that the pencil of electrons with $r = 5$ cm. travelled in a field that was uniform throughout, from target through slit to photographic plate, *i.e.*, the apparatus was so set that the centre of the 5-cm. circle coincided with the centre of the coil system. The accuracy could possibly be improved by working with larger radii of curvature, but it was not practicable for us to use coils much over 40 cm. in diameter, and to work with large radii in the field of small coils involves using unduly large, and correspondingly objectionable, corrections for variation of field along the path. The corrections used in the present work were very thoroughly tested over the whole of the measurable length of the photographic plate (5–6 cm.) by photographing suitable strong lines in a number of different fields, giving a good range in the mean effective values of r.

To reduce the possibility of errors due to movement of the photographic plate in its holder or to distortion of the emulsion during development or fixing, four fiducial marks—two spots and two straight lines—were made on each plate. The spots were produced by exposure to a lamp immediately after the insertion of the plate in the holder, and the lines were formed during the course of the experiment by the action of scattered and straggled electrons, which was limited near the two ends of the plate by straight edges against which the sensitive surface was pressed by the retaining screws. As the fiducial marks were well distributed along the plate, it would have been possible to detect effects either of general movement or local distortion. The results of this test were entirely satisfactory—no plate had to be rejected as a result of unauthorized movement.

The horizontal dimensions of the plateholder and the positions of the fiducial marks were measured on a Lucas co-ordinate comparator, reading to 0·001 cm. by estimation of tenths of divisions on a very open scale. The scale was tested against standard length rods kindly lent to us by Professor E. H. Lamb. The one relevant vertical dimension of the plateholder (vertical distance, upper surface of photographic plate to plane of slit, about 2 cm.) was obtained by an ordinary travelling vernier microscope with horizontal and vertical travel, and by a screw gauge. No very high accuracy is required in this measurement, as an error here of 0·2 mm. only introduces an error of 1 part in 2500 in the measurement of a 5-cm. radius of curvature. The plates themselves were measured on the same comparator, and, with plates taken under sufficiently definite conditions (*v. infra,* § 4), differences larger than 0·005 cm., either in individual measurements of any moderately strong line or in the measurements of the same line on different plates taken with the same field, were quite exceptional.

The current through the Helmholtz coils during an experiment was measured in the usual way, with potentiometer and standard resistance (N.P.L. standardized), and was kept constant to within about 1 part in 10,000 by continuous hand regulation of paralleled sliding rheostats, connected in series with the coils.

§ 3. *Results.*—The results are derived as follows and arranged in Tables I–IV below. The product $r\mathrm{H}$ is obtained directly from the measurements, in gauss cm. The corresponding kinetic energy, W, is deduced from $r\mathrm{H}$ by the relativity formula, assuming values for e and e/m_0. Then W must be divided by h to give the equivalent quantum frequency, ν. As the X-ray spectroscopic results are generally given in terms of (wave number ÷ Rydberg number), it is most convenient for comparison if we also divide our equivalent ν by $c\mathrm{R}$. In what follows, therefore, we express the secondary cathode-ray energies in terms of the X-ray spectroscopists' customary units of "ν/R" (really $\nu/c\mathrm{R}$). In the tables, we denote it by ν^*/R to distinguish it from the corresponding value of ν/R obtained from X-ray spectral data. We quote also this latter value for comparison.

The extraneous errors affecting the two sets of results (ν^*/R and ν/R) are discussed in detail in 'R.P.M.' The "photoelectric" results depend on the assumption of values of e/m_0 and e/h,[†] while the "spectroscopic" results depend on an agreed value for the effective lattice constant of the crystal (calcite or rock salt).

[†] ν^*/R contains a factor approximately equal to $e/m_0 \times e/h$.

Table I.—Gold (79) (metal).

Level values (Siegbahn)—

M_I	252·2	N_I	55·8
M_{II}	231·8	N_{II}	47·3
M_{III}	201·9	N_{III}	39·9
M_{IV}	168·6	N_{IV}	25·8
M_V	162·2	N_V	24·5

Intensity.	rH.	ν^*/R.	Identification.	ν/R (X-ray data).	$\frac{\nu^*-\nu}{R} = \Delta\nu/R$.	$\Delta\nu/\nu^*$ %
2	229·9	342·1	Cu $K\alpha_1$—Au M_I	340·5	1·6	0·47
2–3	236·8	362·8	$K\alpha_1$— M_{II}	360·9	1·9	0·52
6	246·4	392·8	$K\alpha_1$— M_{III}	390·8	2·0	0·51
6	256·8	426·2	$K\alpha_1$— M_{IV}	424·1	2·1	0·49
6	258·7	432·7	$K\alpha_1$— M_V	430·5	2·2	0·51
1–2	277·3	496·6	$K\beta_1$— M_V	493·7	2·9	0·58
4	289·3	540·0	$K\alpha_1$— N_I	536·9	3·1	0·57
4	291·5	548·3	$K\alpha_1$— N_{II}	545·4	2·9	0·53
4–5	293·5	555·8	$K\alpha_1$— N_{III}	552·8	3·0	0·54
5	297·5	570·9	$K\alpha_1$— $N_{IV,\,V}$	568·2	2·7	0·47†

† Complex line.

Table II.—Tungsten (74) (oxide).

Level values (Siegbahn)—

M_I	207·3	N_I	43·3
M_{II}	189·3	N_{II}	36·0
M_{III}	167·5	N_{III}	31·0
M_{IV}	137·5	N_{IV}	18·7
M_V	132·9	N_V	17·6

Intensity.	rH.	ν^*/R.	Identification.	ν/R (X-ray data).	$\frac{\nu^*-\nu}{R} = \Delta\nu/R$.	$\Delta\nu/\nu^*$ %
4	244·6	387·0	Cu $K\alpha_1$—W M_I	385·4	1·6	0·41
4–5	250·3	405·1	$K\alpha_1$— M_{II}	403·4	1·7	0·42
6	257·0	426·9	$K\alpha_1$— M_{III}	425·2	1·7	0·40
5–6	265·9	456·9	$K\alpha_1$— M_{IV}	455·2	1·7	0·37†
5–6	267·4	462·0	$K\alpha_1$— M_V	459·8	2·2	0·48
1	269·6	469·6	$K\beta_1$— M_{II}	466·6	3·0	0·64
1–2	275·7	491·1	$K\beta_1$— M_{III}	488·4	2·7	0·55
1–2	284·1	521·2	$K\beta_1$— M_{IV}	518·4	2·8	0·54
1–2	285·5	526·2	$K\beta_1$— M_V	523·0	3·2	0·61
4	292·6	552·5	$K\alpha_1$— N_I	549·4	3·1	0·56
4	294·4	559·3	$K\alpha_1$— N_{II}	556·7	2·6	0·46
4–5	295·9	564·9	$K\alpha_1$— N_{III}	561·7	3·2	0·57
5	299·3	577·9	$K\alpha_1$— $N_{IV,\,V}$	575·1	2·8	0·49

† Inaccurate, not separated.

Table III.—Silver (47) (metal).

Level values (Siegbahn)—

L_I	282·0	M_I	54·7
L_{II}	261·3	M_{II}	46·1
L_{III}	248·6	M_{III}	43·7
		M_{IV}	29·2
		M_V	28·8

Intensity.	rH.	$\nu^*/$R.	Identification.	$\nu/$R (X-ray data).	$\frac{\nu^*-\nu}{R} = \Delta\nu/R$.	$\Delta\nu/\nu^*$ %
? 3	219·6	312·2	Cu $K\alpha_2$—Ag L_I	309·3	2·9	0·93†
5	220·2	313·9	$K\alpha_1$— L_I	310·7	3·2	1·02
? 3	226·9	333·2	$K\alpha_2$— L_{II}	330·0	3·2	0·96†
5	227·4	334·7	$K\alpha_1$— L_{II}	331·4	3·3	0·99
? 3	231·3	346·2	$K\alpha_2$— L_{III}	342·7	3·5	1·01†
6	231·8	347·7	$K\alpha_1$— L_{III}	344·1	3·6	1·04
1–2	241·7	377·9	$K\beta_1$— L_I	373·9	4·0	1·06
1–2	248·3	398·7	$K\beta_1$— L_{II}	394·6	4·1	1·03
1–2	252·4	411·8	$K\beta_1$— L_{III}	407·3	4·5	1·09
5	290·1	543·2	$K\alpha_1$— M_I	538·0	5·2	0·96
5	292·8	553·3	$K\alpha_1$— M_{III}	549·0	4·3	0·78
2–3	297·1	569·5	$K\alpha_1$— M_V	563·9	5·6	0·98
1–2	309·6	618·0	$K\beta_1$— M_{III}	612·2	5·8	0·94

† Barely separated.

Table IV.—Copper (29) (metal).

Level values (Siegbahn)—

L_I	81·0
L_{II}	70·3
L_{III}	68·9

Intensity.	rH.	$\nu^*/$R.	Identification.	$\nu/$R (X-ray data).	$\frac{\nu^*-\nu}{R} = \Delta\nu/R$.	$\Delta\nu/\nu^*$ %
6	282·3	514·4	Cu $K\alpha_1$—Cu L_I	511·7	2·7	0·53
4	285·6	526·6	$K\alpha_1$— L_{III}	523·8	2·8	0·53†

† Complex line.

The "intensities" listed in the tables are rough visual estimates of the relative photographic intensities, graded 1 to 6 in increasing order. No stress is laid on them here; they are inserted merely as an indication of each type of line being measured—a strong line can naturally be measured with greater certainty than a faint one. Where the intensity is queried the line is partially obscured by the "spread" on the low-velocity side of a neighbouring strong line of slightly greater velocity. (It will be recalled that, with the focussing method used in this work and with the use of targets of finite thickness, if we have two groups of electrons differing only slightly in velocity, the trace of the slower group may be obscured by that of the faster.)

In compiling the tables, we have taken the X-ray data from the last edition of Siegbahn's standard treatise.[†] In working out our own results, we have taken

$$e/m_0 = 1\cdot759 \times 10^7 \text{ e.m.u. gm.}^{-1}$$

and

$$e/h = 7\cdot290 \times 10^{16} \text{ e.s.u. erg.}^{-1} \text{ sec.}^{-1}.\ddagger$$

The reasons for taking these values are set out in 'R.P.M.' They appeared to correspond to a reasoned average of the most reliable observations made by methods largely independent of X-ray measurements, and it is, therefore, of interest to compare them with the X-ray data. The magnitudes of the permissible adjustments of these values of e/m_0 and e/h will be briefly considered in the sequel.

The frequencies of the primary X-rays used in this work, in Rydberg units, are :—

Cu	$K\alpha_1$	592·7
	$K\alpha_2$	591·3
	$K\beta_1$	655·9

§ 4. *Discussion.*—To facilitate comparison of the "photoelectric" and "spectroscopic" values, we have, in the last column of the tables, expressed $\frac{\nu^*}{R} - \frac{\nu}{R} = \frac{\Delta\nu}{R}$ as a percentage of ν^*/R. It will be seen that ν^*/R is greater than ν/R by approximately 0·5% (1% for silver, but we shall give reasons later for possibly modifying this figure). It will be realized that this method of writing the results is very sensitive to the effects of small errors in rH, as well as to those of slight variations in the X-ray data.

We have also a number of results from photographs obtained with oxides of the two rare earths, lanthanum and neodymium. For both the ν^*/R

[†] Siegbahn, "Spektroskopie der Röntgenstrahlen," 2nd ed. (Berlin, 1931), Tables 176A and 176B (pp. 346 ff.).

[‡] From $h = 6\cdot543 \times 10^{-27}$ erg. sec., and $e = 4\cdot770 \times 10^{-10}$ e.s.u.

values were slightly *smaller* than the ν/R, but we can have no confidence in these results, as the values obtained with different fields, and with the same fields in different exposures, were very far from consistent. We finally traced down the unexpectedly high insulating power of the targets as the almost certain cause of these discrepancies. We normally use targets mounted direct on a thin aluminium slip which is in metallic connection with the plateholder and with the whole of the camera case. For the rare earth targets, where supplies of the material were very limited, we mounted slips of thin, fine-grained filter paper on the aluminium and deposited a layer of oxide, from suspension in alcohol, on the surface of the paper. Later tests with a gold-leaf electroscope showed these layers to be highly insulating, even in normal, not very dry air. This property would most probably be still more pronounced under the conditions of an experiment, in the highly evacuated camera, and it seems very likely that the targets could become charged up to positive potentials of the order of 50 volts, even with the comparatively feeble electron currents then drawn from them. We mention this matter in some detail, as it seems possible that others engaged in similar work may encounter troubles of the same kind.

We have not repeated the work with lanthanum and neodymium for the purpose of this communication—the experiments with these elements were, in fact, originally undertaken as part of a special examination of the rare earths, which has now been postponed. The rare earths are not very suitable for the present comparison, as it seems clear, from inspection of the available data on their emission lines and absorption edges, that the X-ray spectra need re-investigation.

We can, therefore, for two reasons attach no weight to the different sign obtained for $\Delta\nu/\nu^*$ for these two elements—especially as it is a difference exactly of the kind to be expected if the target charges up to a positive potential during the experiment. It is, however, worth mentioning that we were successful in photographing electrons ejected from the L_{II} and L_{III} levels of neodymium and from all three L levels of lanthanum, in every case sufficiently clearly to show the separation of the groups due to the two components of the Cu Kα doublet. For Nd L_{II}, this means photographing faint lines with energies no higher than 95 Rydberg units (say, about 1300 electron volts), and we have measured other ("fluorescent"†) lines down to 700 electron volts. Although we cannot use these results here, the successful photography of these low-speed groups is distinctly promising in connection with projected extensions of the present work.

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† We use the term "fluorescent" lines as a convenient abbreviation for lines due to groups of photoelectrons of the second kind.

We ought also to add that, in addition to those given in the tables, we have measured a number of other strong lines—some "fluorescent," others secondary cathode rays from levels so closely packed in the scheme that no unambiguous interpretation of their origin can be put forward. There is no point in listing them here, but all were accurately measured, and in a number of cases they served as valuable reference lines in cross-checking from one magnetic field to another and in testing the corrections for inhomogeneity of field.

Returning now to the consideration of Tables I–IV, there are a few points to be mentioned, particularly about the X-ray data. In gold, the ν^*/R values are very consistently and uniformly higher than the corresponding ν/R. We have no details of the experimental data from which Siegbahn compiled this part of his table, but his values are in much better agreement (or, we should rather say, in more consistent disagreement) with our results than are the values in any earlier published table. One of us had previously noticed, in particular, that, in the photoelectric work, the M_{II} level of gold came out somewhat anomalously, as compared with the other four M levels; this was, in fact, one of the anomalies referred to in 'R.P.M.,' p. 609, which had been marked down for further investigation. In his latest table, Siegbahn has changed M_{II} from 235·1 to 231·8 Rydbergs, which brings this level into line with our measurements of the other levels.

With tungsten and copper, which have been, for obvious reasons, standard anticathode materials in X-ray research for many years, it does not seem likely that there can be any serious error in the X-ray data. Our results for tungsten were obtained with an oxide target (they will be repeated later with a target of the element) and are based on a smaller number of plates than were taken for the other elements. The results were, however, remarkably consistent and we do not think they can be seriously in error. In particular, there was no evidence, either in the measurements or in a test with the electroscope, of effects similar to those experienced with Nd and La.

With silver, where the results are out of line with those for the other three elements, it is worth noting that, if we use term values for L_I, L_{II}, L_{III} obtained by direct measurement of absorption edges, the first part of Table III becomes as in Table IIIA.

If the Van Dyke and Lindsay, *loc. cit.* values are accepted for the silver L levels, the tabulated M (and K) levels will also have to be adjusted in the same sense. An adjustment of the M level values in this sense would be an improvement from the point of view of our work; there is, of course, no direct evidence as to their most probable values. The adjustment required in the K level corresponds to a displacement of just over 0·4 X.U. in the position of the K absorption edge—little more than the difference between the measurements of Enger and of Leide. We shall, therefore, provisionally accept Van Dyke and Lindsay's values for the L levels, which are also more in harmony with the results of Kretschmar.†

We may say, then, that our results indicate fairly consistently a difference of 0·5% between the "photoelectric" and the "spectroscopic" values of ν/R, the former being the greater. An error of 1 part in 1000 one way or the other in the values of rH would change this to 0·3% or 0·7%. We believe that our errors are smaller than 1 part in 1000 and that our results may be taken as showing at least that the difference between ν^*/R and ν/R lies between 0·4% and 0·6%. We shall think of it for the present as being 0·5%. The difference is in the sense already indicated in the earlier work of Robinson, in which, however, it was clearly underestimated (*cf.* 'R.P.M.,' pp. 605, 612). Kretschmar's results show exactly the same type of difference; his

Table IIIA.—Silver.

Level values (Van Dyke and Lindsay‡)—

L_I 280·6
L_{II} 259·9
L_{III} 246·9

Intensity.	rH.	ν^*/R.	Identification.	ν/R (X-ray data).	$\frac{\nu^* - \nu}{R} = \Delta\nu/R$.	$\Delta\nu/\nu^*$ %
? 3	219·6	312·2	Cu $K\alpha_2$—Ag L_I	310·7	1·5	0·48†
5	220·2	313·9	$K\alpha_1$— L_I	312·1	1·8	0·57
? 3	226·9	333·2	$K\alpha_2$— L_{II}	331·4	1·8	0·54†
5	227·4	334·7	$K\alpha_1$— L_{II}	332·8	1·9	0·57
? 3	231·3	346·2	$K\alpha_2$— L_{III}	344·4	1·8	0·52†
6	231·8	347·7	$K\alpha_1$— L_{III}	345·8	1·9	0·55
1–2	241·7	377·9	$K\beta_1$— L_I	375·3	2·6	0·69
1–2	248·3	398·7	$K\beta_1$— L_{II}	396·0	2·7	0·68
1–2	252·4	411·8	$K\beta_1$— L_{III}	409·0	2·8	0·68

† Barely separated.

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† *Loc. cit.* It is, perhaps, not out of place to point out that, in respect of systematic X-ray spectroscopy, silver is amongst what may be called the "transition elements"—it falls in the region in which it is not easy to decide whether to base data on the K or the L edges as the primary standards.

‡ 'Phys. Rev.,' vol. 30, p. 562 (1927).

values of $r\mathrm{H}$ are appreciably higher than the corresponding earlier ones of Robinson and Cassie, but, so far as they can be compared, *i.e.*, only indirectly, with our present results, they indicate a slightly smaller excess of ν^*/R over ν/R.

The question of the accuracy of the absolute values of the X-ray wave-lengths will probably be settled finally by the beautiful work now proceeding in Siegbahn's laboratory. Pending decisive results from this source, we shall probably not be far wrong in assuming that the X-unit is very close to $1\cdot001 \times 10^{-11}$ cm.[†] Then, all the X-ray terms and frequencies must be reduced by $0\cdot1\%$—which increases the discrepancy between the "photoelectric" and "spectroscopic" values to about $0\cdot6\%$.

To bring the two sets into the sort of agreement which might reasonably be expected, we require, then, in effect, to find how the value we have adopted for the product $e/m_0 \times e/h$ can be reduced by at least $0\cdot4$-$0\cdot5\%$. It appeared until quite recently that the downward trend of the "deflection" value of e/m_0 must cease with its almost asymptotic approach to the accepted "spectroscopic" value of this constant. The latest reported direct electrical measurement of e/m_0—that of Dunnington[‡]—is, however, lower still, viz. $(1\cdot7571 \pm 0\cdot0015) \times 10^7$ e.m.u. gm.$^{-1}$. This, by a coincidence, is almost identical with the mean value obtained by Kretschmar $(1\cdot7570 \times 10^7)$ and published independently in the same number of the 'Physical Review.' Kretschmar bases this value on the assumption $h/e = 1\cdot3737 \times 10^{-17}$ erg. sec. e.s.u.$^{-1}$, and he points out that Duane, Palmer, and Yeh's value of $1\cdot3751 \times 10^{-17}$ gives $e/m_0 = 1\cdot7588 \times 10^7$ from the same data.

If we may accept the lowest quoted value of e/m_0, this reduces appreciably the adjustment required in the value of e/h. The value we adopted above (which corresponds to $h/e = 1\cdot3717 \times 10^{-17}$) is definitely high as compared with the results of the X-ray short-wave limit measurements. If we take $e/m_0 = 1\cdot757 \times 10^7$ and $h/e = 1\cdot375 \times 10^{-17}$, this reduces the discrepancy between ν^*/R and ν/R to approximately $0\cdot2\%$, even after making allowance for the probable error in the absolute values of the X-ray wave-lengths. It is, however, difficult to reconcile these values with the data from precise measurements of other relations between the constants, and nothing can be usefully added here to the very full discussions of the general problem which have been published by Birge and others.

[†] Kretschmar avoids a part of this particular difficulty by using a value of h/e obtained in direct X-ray experiments (inverse photoelectric effect) involving the calcite spacing.

[‡] 'Phys. Rev.,' vol. 43, p. 404 (1933).

We can, however, arrive at the result we require in a much less ingenuous fashion, without making use of any of the measurements of h. We need, in fact, only consider the values of the constant of the Compton shift and of e/m_0, both of which have recently been very accurately measured. Gingrich[†] finds for the first of these constants 24·24 X.U., which we shall write as $2\cdot426 \times 10^{-10}$ cm., to be consistent with our previous treatment of the X-ray wavelengths. For e/m_0, we have Kirchner's[‡] very accurate work, leading to the value $1\cdot7585 \times 10^7$ e.m.u./gm., which is in excellent accord with the "spectroscopic" values (*cf.* data in 'R.P.M.'). We have then

$$h/e = \left(\frac{h/m_0c}{e/m_0}\right)^{\S} = \frac{2\cdot426 \times 10^{-10}}{1\cdot7585 \times 10^{7}} = 1\cdot3796 \times 10^{-17} \text{ erg. sec. e.s.u.}^{-1},$$

a value which exactly reconciles our results with the X-ray data when we use with it again, as, of course, we must, Kirchner's e/m_0.

These last values give us, in fact, for the product $(e/h \times e/m_0)$ a figure exactly $0\cdot60\%$ smaller than that used in compiling Tables I to IV. From the mode of derivation, it will be clear that the error in the product $(e/h \times e/m_0)$ is compounded of (*a*) the error in the measurement of the Compton shift, and (*b*) the error in the value of $(e/m_0)^2$. The other available accurate measurement of the Compton shift—Sharp's[||] value of 24·32 X.U.—would carry us still farther away from the figures first used.

Perhaps we ought not to lay too much stress on the agreement between our results and the data derived from the Compton shift. There is, however, one remarkable recent determination of practically the same quantity, namely, Meibom and Rupp's[¶] measurement, by diffraction in a film of gold, of the de Broglie wave-length of fast electrons. The quantity measured is, of course, $\lambda = h/mv$; the velocity was measured accurately in Kirchner's e/m_0 apparatus (*loc. cit.*).

Meibom and Rupp used their measurements actually to obtain a value for h/e by means of the relation

$$h/e = \frac{\lambda v}{e/m_0\sqrt{1-\beta^2}}.$$

Using Kirchner's e/m_0, they found $h/e = 1\cdot3798 \times 10^{-17}$ (with a probable

[†] 'Phys. Rev.,' vol. 36, pp. 364, 1050 (1930).

[‡] 'Ann. Physik,' vol. 8, p. 975 (1931); vol. 12, p. 503 (1932).

[§] We follow current practice in keeping e in e.s.u., except when dealing with the ratio e/m_0, when we quote e in e.m.u.

[||] 'Phys. Rev.,' vol. 26, p. 691 (1925).

[¶] 'Ann. Physik,' vol. 13, p. 725 (1932).

error in the measurements of about ±0·3%). This is in remarkable agreement with the value deduced from the Compton shift—in fact, if we use Meibom and Rupp's mean value, we can deduce exactly $2\cdot626 \times 10^{-10}$ cm. for the Compton constant.

Again, we must not lay too much weight on these figures; the remarkable agreement down to "significant" figures which we clearly have no right to retain cannot be other than fortuitous. The electron diffraction experiments are obviously difficult ones, and the authors point out that they have to assume that the effective grating space of a gold film for fast electrons is identical with that of a thicker plate for X-rays. The exact agreement between the results, of these two closely analogous experiments—one based on the scattering of electrons, the other on the scattering of photons—has, so far as we know, never been pointed out. It may be no more than a coincidence, but at least it is a coincidence which invites attention and, in view of our own results in an entirely different field, we are naturally inclined to give it prominence.

We have pleasure in acknowledging our indebtedness to the Government Grant Committee of the Royal Society for grants which covered the cost of a great part of the apparatus and materials used in this work, and to Professor E. H. Lamb for supplies of liquid air.

Summary.

New measurements have been made of the energies of the groups of homogeneous secondary cathode rays expelled from gold, tungsten, silver, and copper by the K series X-rays of copper. The results are compared, in the light of recent determinations of the fundamental atomic constants, with the values to be expected from X-ray spectroscopic data, and it is shown that they are consistent with the observed value of the constant of the Compton shift and with recent work on electron diffraction, rather than with the accepted values of h and e.

Reaction Kinetics in Films. The hydrolysis of γ-Stearolactone.

By Russel J. Fosbinder and Eric K. Rideal, F.R.S., Colloid Science Laboratory, Cambridge.

(Received August 10, 1933.)

In previous communications* it was shown that it was possible from observation of the phase boundary potential to study the kinetics of reactions proceeding at air liquid interfaces. A chemical change occurring in a unimolecular film at an air liquid interface may result in (*a*) a change in the magnitude of the vertical component of the apparent electric moment of the film-forming molecule, as observed in the oxidation of unsaturated acids; (*b*) an aggregation due to greatly reduced adhesion as in the spontaneous oxidation of long chain mercaptans to form disulphides; or (*c*) the diffusion of the product away from the surface as is the case in the hydrolysis of γ-stearolactone.

A consideration of such heterogeneous systems reveals several factors of interest in the sphere of reaction kinetics. In some instances it is evident that the velocity of the process may be governed by the rate of diffusion of products away from the surface rather than by the rate of the chemical reaction. If the chemical process is the slower, then it will determine the velocity of the reaction. In a surface reaction, not complicated by diffusion, the velocity would be determined by the collision frequency, the probability of energy transfer involved in activation, and an orientation factor. This latter factor of molecular orientation, doubtless present in many heterogeneous catalyses, is clearly defined in the oxidation of films of unsaturated acids, and as it will be shown an alteration in the inclination of the polar group results in a significant change in the reaction velocity constant, also in the hydrolysis of the lactone.

An investigation by the method of phase boundary potentials of the hydrolysis of γ-stearolactone on the surface of moderately concentrated sodium hydroxide solutions has yielded information relative to the kinetics and mechanism of the reaction, permitting an application of the kinetic theory to the results of the experiments.

The results of surface potential measurements on stable films of the lactone and the corresponding γ-hydroxy acid can likewise be interpreted in terms of the behaviour of the molecules of the γ-hydroxy acid toward thermal agitation and chemical reaction of the lactone ring with the substrate.

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* Hughes and Rideal, 'Proc. Roy. Soc.,' A, vol. 140, p. 253 (1933).

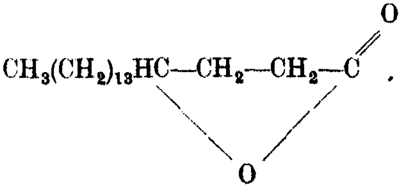
Experimental.

The phase boundary potential measurements were made according to the method described by Schulman and Rideal.* A modified apparatus was employed in that the metal box was replaced by a double walled copper box, through which water from a thermostat was circulated in order to maintain the liquid in the trough, and the polonium electrode at any desired temperature. The Lindemann electrometer was placed in a metal box outside the thermostat. In working with solutions of hydrochloric acid a silver-silver chloride electrode or calomel cell with a bridge was used while a silver plate served as a reference electrode when solutions of caustic soda were employed.

Measurements of the two dimensional surface pressure of the films were made on a Langmuir trough sensitive to 0·25 dyne/cm.

The solvent used in spreading films of the lactone was 60°–80° C. petrol ether, while chloroform or an alcohol-petrol ether mixture was employed as a solvent for the hydroxy acid. The volume of the liquid dropped upon the surface was measured by means of an "Agla" micrometer syringe.

γ-stearolactone and the hydroxy acid were prepared by the methods described by Clutterbuck,† the specimens having the following structures and melting points :—

Compound.	Structure.	Melting point. °C.
γ-stearolactone		50
γ-hydroxystearic acid	$CH_3(CH_2)_{13}CHOH(CH_2)_2COOH$	84

Results of Experiment.

γ-hydroxystearic Acid.—A series of force-area curves were obtained for the acid on N/100 HCl, the temperature of the substrate varying from 4° to 33° C. The results are shown in fig. 1.

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* 'Proc. Roy. Soc.,' A, vol. 130, p. 259 (1931).

† 'J. Chem. Soc.,' vol. 75, p. 2330 (1924).

At 4° C. the film is almost completely condensed, while at higher temperatures the curves resemble those obtained for fatty acid films in the liquid expanded state with the transition to the condensed form at high pressures. At 33° C. the film was not completely expanded. The area per molecule for the expanded film extrapolated to zero compression was 60 A.^{2} which is greater than that obtained for the limiting areas of myristic acid and oleic acid. With a surface pressure of 1·5 dynes per centimetre the temperature of half expansion was found to be 9° C. On N/10 and on N . NaOH solutions the acid did not spread to form a film, due either to aggregation or solution of the substance.

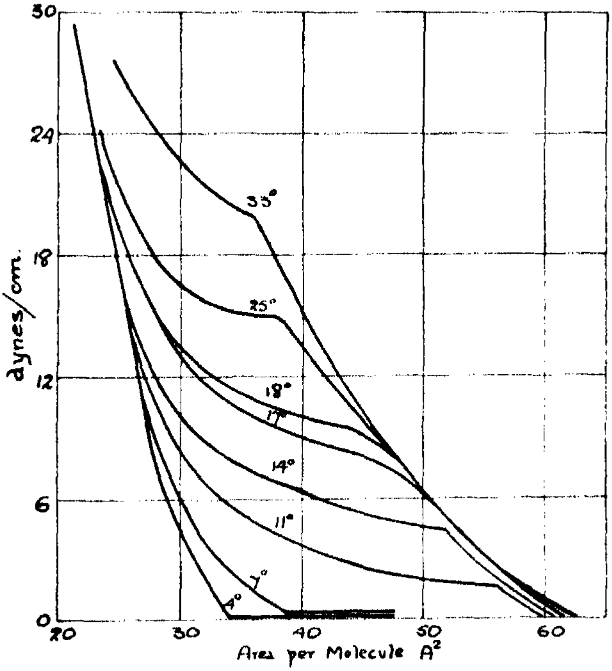


FIG. 1.—γ-hydroxystearic acid, N/100 HCl.

In view of some experiments to be mentioned in connection with the hydrolysis of the lactone it appears that the acid rapidly undergoes solution on very alkaline substrates.

In fig. 2 is shown the change in the vertical component of the electric moment (μ) with the variation in the molecular area of a film of hydroxy acid on N/100 HCl at various temperatures. At 17·5° C. the potential over the surface was uniform when the values of the area per molecule (A) and ΔV were respectively 60 A.^{2} and 158 mv. When the temperature of the substrate was decreased to 5° C. the corresponding values for A and ΔV were 37·7 A.^{2} and

255 mv. The values of the electric moment obtained from the limiting values of ΔV at various temperatures (that is, when the film is first uniform) were found to be constant and equal to $2 \cdot 55 \times 10^{-19}$ e.s.u. A straight line connecting the limiting values was found to pass through the origin and the value of μ obtained from the slope was $2 \cdot 55 \times 10^{-19}$ e.s.u. It would thus appear that this value represents the true magnitude of the contribution of the relative electric moment of a molecule of γ-hydroxystearic acid in the expanded state.

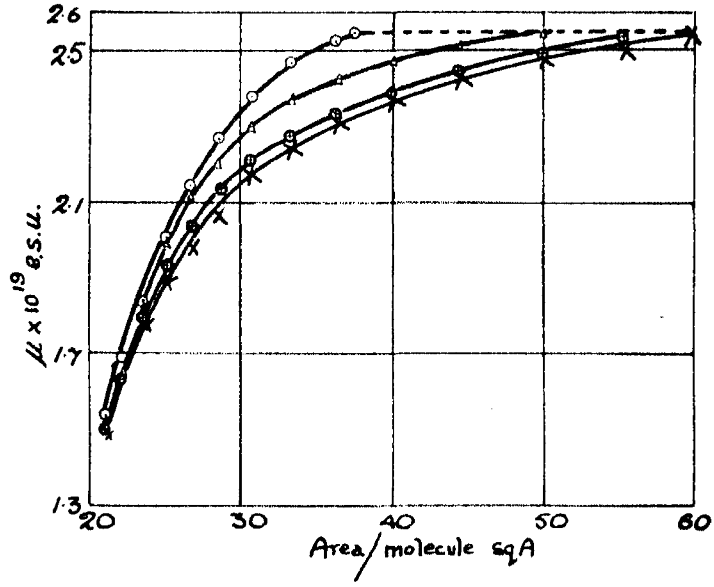


FIG. 2.—γ-hydroxystearic acid on N/100 HCl.
×, 17·5° C.; ⊕, 13° C.; Δ, 10° C.; ⊙, 5° C.

Assigning the value of $1 \cdot 80 \times 10^{-19}$ e.s.u. per molecule for the carboxyl group and assuming the dipole moment to be additive, a value of $0 \cdot 75 \times 10^{-19}$ e.s.u. is obtained for the $>$CHOH group. This is approximately one-fourth the value found by Hughes and Rideal (*loc. cit.*) for two adjacent OH groups in the initial oxidation products of petroselinic and oleic acids. The small value obtained for the electric moment suggests a lateral attraction between the nearby polar groups imparting a more horizontal position to the $>$CHOH group.

In this connection it is of interest to note the values of μ as a function of the molecular area. On compression of the films to $20 \cdot 6$ square A. it is seen that the value of μ decreases from the limiting value of $2 \cdot 55 \times 10^{-19}$ e.s.u. to $1 \cdot 53 \times 10^{-19}$ e.s.u., the latter being approximately equal to the value of μ for a fatty acid molecule in the condensed state ($1 \cdot 56 \times 10^{-19}$ e.s.u.). Further, it is to be noted that the rate of change of the electric moment with molecular area decreases as the temperature increases. These facts clearly show that on compression of an expanded film of γ-hydroxystearic acid the $—CHOH—CH_2—CH_2$ group is removed from the surface.

If, at a given area per molecule the thermal energy of agitation be sufficient to overcome the adhesive forces by which a certain number of the $>CHOH$ groups are anchored to the surface, then one would anticipate that the apparent molecular electric moment would decrease exponentially with an increase in temperature until a critical temperature is reached. It was found that the observed variation in μ with temperature for a series of values in which (*n*) varied from 2·5 to $3 \cdot 63 \times 10^{14}$/sq. cm. could be represented by an equation of the Boltzmann type

$$M_A = M_O e^{-\frac{\phi}{KT}}, \qquad (1)$$

where M_A = the vertical component of the electric moment of a gram molecule of γ-hydroxy acid at a given molecular area, $M_O = 2 \cdot 55 \times 10^{-19} \times 6 \cdot 06 \times 10^{23}$ e.s.u., and ϕ = the change in potential to kinetic energy when 1 gram mol of $>CHOH$ leaves the surface.

The average value of ϕ obtained by plotting $\log_e M_A/M_O$ against $1/T$ was found to be 1500 cal. per gram mol. The energy change thus associated with the removal of one $>CHOH$ group from the aqueous surface to a hydrocarbon environment is $\frac{1500 \times 4 \cdot 2 \times 10^7}{6 \cdot 06 \times 10^{23}} = 10 \cdot 4 \times 10^{-14}$ ergs. We may compare this value with the energy required for the spreading of an alcohol when a drop of the liquid is placed on the surface of water. Harkins obtained for the spreading coefficient of octyl alcohol on water, *i.e.*, the work of adhesion minus the work of cohesion, a value of 36·7 ergs./sq. cm. Assuming the alcohol molecule to occupy an area of 25 A.^{2} in the Gibbs layer, the energy required for the spreading of a single molecule is $\frac{36 \cdot 7}{4 \times 10^{14}} = 9 \cdot 2 \times 10^{-14}$ ergs. The good agreement between the values of the energy of spreading obtained from surface tension measurements, and from the temperature coefficient of the molecular electric moment, supports the view that a removal of the $—CH_2CH_2CHOH$ group from the water surface is involved when a film of γ-hydroxy acid is subjected to compression.

γ-*stearolactone*.—At temperatures below 20° C. on N/100 HCl the area per molecule for a condensed film of lactone extrapolated to zero compression was 30 A.^{2}, a value in good agreement with those previously determined. Above

20° C. the films are partially expanded at low pressures. A surface pressure of 30 dynes/cm. reduced the area per molecule to 24·5 A.^{2}.

The results of the surface potential examination of lactone films on various substrates are shown in fig. 3. On N/100 HCl, N/100 and N/10 NaOH solutions the film became uniform in potential at molecular areas below 31 A.^{2}. In the case of 4 N.HCl an expansion was noted, the film being uniform at an area of 34·5 A.^{2}. From fig. 3 it is seen that the surface potentials and the slopes of the $\Delta V/n$ curves vary with the p_H of the underlying solution. In order to obtain more information concerning the influence of the substrate on the polar head group, equilibrium spreading values of the potentials ($\Delta V\alpha$) were determined. In Table I the molecular electric moments obtained from the slope of the $\Delta V/n$ curves and the corresponding $\Delta V\alpha$ values are given.

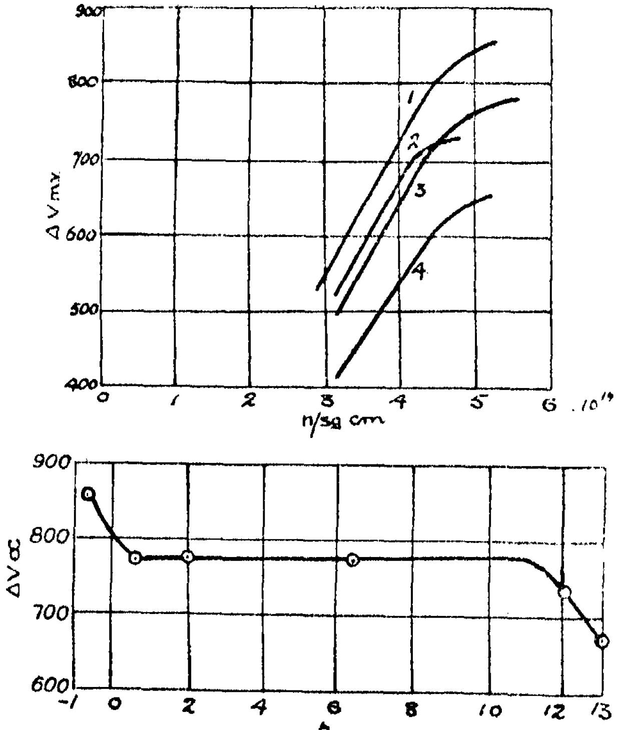
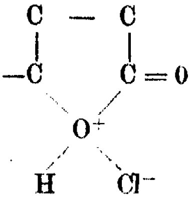
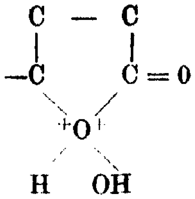


FIG. 3.

$\mu \times 10^{19}$	on	
1. 4·83	0·4 N . HCl.	
2. 4·58	0·01 N . NaOH	t = 18°–19° C.
3. 4·58	0·01 N . HCl.	
4. 3·72	0·1 N . NaOH.	

The observed increase in surface potential and $\bar{\mu}$ on 4 N . HCl and the decrease in both values on N/10 NaOH is similar to the behaviour of a long chain alcohol on substrates over a wide p_H range as noted by Schulman and Hughes.* The change in $\bar{\mu}$ may be attributed to the formation of an ionized complex on concentrated HCl, and the formation of an oxonium compound on alkali, as indicated below :—





The addition of a water molecule to the lactone ring as postulated above permits one to visualize the mechanism of the ring scission for the complex is able to donate a hydrogen ion to the proton acceptor, the OH′ ion.

Table I.—T = 18° C.

Substrate.	$\bar{\mu} \times 10^{-18}$ e.s.u.	ΔVa (mv.).
4 N . HCl	4·83	860
N/100 HCl	4·58	774
N/100 NaOH	4·58	734
N/10 NaOH	3·72	669

The Hydrolysis of γ-stearolactone.

As shown by Adam† a film of lactone on the surface of N . NaOH rapidly undergoes hydrolysis with the formation of γ-hydroxystearic acid. By means of the surface potential method it was found that at room temperature the value of ΔV initially about 550 mv. decreased rapidly, finally approaching the potential value of the aqueous surface after 2 hours had elasped. Further, the curve obtained by plotting observed values of ΔV against the time resembled that of a unimolecular reaction.

If one assumes the unimolecular law and (n) is the number of molecules initially present and n_1 the number present at "t" with electric moment μ, then

$$\Delta V_t = 4\pi\mu n_1,$$

---

* 'Proc. Roy. Soc.,' A, vol. 138, p. 430 (1932).

† 'Proc. Roy. Soc.,' A, vol. 140, p. 223 (1933).

and since

$$\frac{dn_1}{dt} = kn_1,$$

then

$$\frac{d\Delta V}{dt} = 4\pi\mu \frac{dn_1}{dt} = k\, 4\pi\mu n_1$$

$$\frac{d\Delta V}{dt} = k\Delta V_t,$$

integrating

$$kt = -\log \Delta V_t + C$$

when $t = 0$

$$\Delta V_t = \Delta V_0$$

and

$$k = -\frac{1}{t}\, ln \frac{\Delta V_0}{\Delta V_t} \quad \text{or} \quad k = \frac{1}{t}\, ln \frac{\Delta V_0 - \Delta V_\infty}{\Delta V_t - \Delta V_\infty}\,. \tag{2}$$

In applying the equation given above to the experimental results the slope of the curve obtained by plotting the observed values of $\log_{10}(\Delta V_t - \Delta V_\infty)$ against the time is equal to 0·4343 k. An alternative form of the unimolecular expression, namely,

$$-k = \frac{1}{\Delta_t}\, ln \frac{\Delta V_{t+\Delta t} - \Delta V_\infty}{\Delta V_t - \Delta V_\infty} \tag{3}$$

may be conveniently used in which the appropriate values are obtained directly from the $\Delta V - t$ curve for equal time intervals.

Application of equations (2) and (3) to the experimental results gave values of k which were in good agreement.

Although the change in ΔV with time, when substituted in the above expressions, for a single experiment, gave a unimolecular constant, it is evident that the reaction is in reality bimolecular as we are considering the interaction of lactone hydrate with the OH′ ion. Under the conditions of experiment the true expression for the velocity constant is

$$k_2 = \frac{1}{bt}\, ln \frac{\Delta V_0 - \Delta V_\infty}{\Delta V_t - \Delta V_\infty}\,,$$

where k_2 is the bimolecular velocity constant and b the concentration of OH ions in the substrate.

Values of k_2 were determined for the conversion of lactone to acid on 1 N NaOH at various temperatures, the results of which are given in Table II.

If the reaction velocity increases exponentially with the temperature, the relation between k, T, and E the apparent energy of activation is given by the expression

$$\frac{d \ln k}{dt} = \frac{E}{RT^2}, \tag{4}$$

which in the integrated form becomes

$$2 \cdot 303 \log k = \frac{-E}{RT} + C.$$

On plotting the observed values of $2 \cdot 303 \log k$ against 1/T as shown in fig. 4. curve *a*, a straight line was obtained.

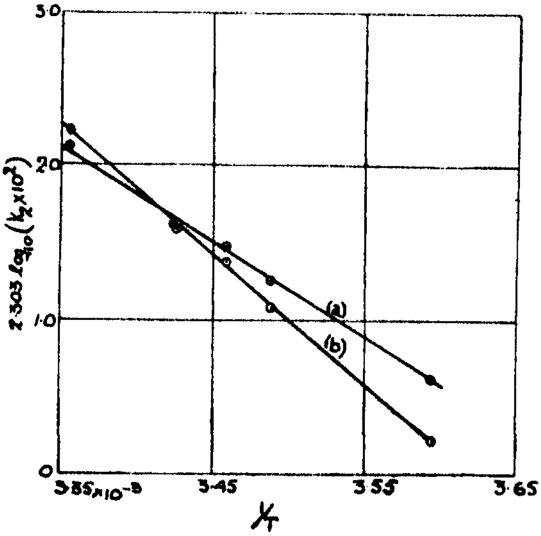


FIG. 4.—(*b*) $2 \cdot 303 \log_{10} (k_2 \times 10^2)$ against 1/T.

Table II.—$n_0 = 3 \cdot 35 \times 10^{14}$ mols./sq. cm. k_2 = litres/gm. mol./min.

t°.	$k_2 \times 10^2$.
5·0	1·88
13·5	3·55
16·0	4·48
19·0	5·06
25·0	8·40

From the slope of the curve a value of E = 12,500 calories per gm. mol. was found and from this the temperature coefficient of the reaction, $k_{35^\circ}/k_{25^\circ} = 1 \cdot 98$. The corresponding values for the reaction between the lactone molecule in solution and the alcoholate ion in solution, obtained from

Clutterbuck's data (*loc. cit.*) are 11,200 calories/gm. mol. and $dk/dT = 1 \cdot 84$ respectively. It is of interest to note that the temperature coefficient of the surface reaction is a mean of those usually ascribed to catalysis by hydrogen and hydroxyl ions.

In fig. 5 the reaction velocity at 25° C. and at constant lactone concentration (4×10^{14} mol./sq. cm.) is plotted against the moles/litre of NaOH. It is seen that the reaction is bimolecular, also that the velocity varies in a linear manner with the NaOH concentration. The value of k_2 obtained from the slope of the curve is $8 \cdot 4 \times 10^{-2}$ litres/gm. mol./min.

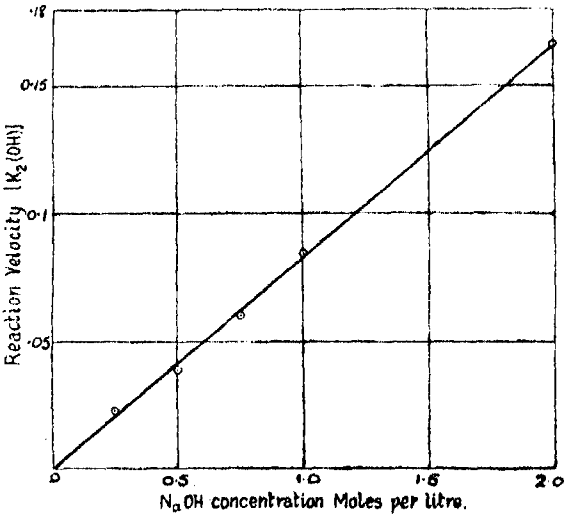


Fig. 5.

A series of experiments were carried out maintaining the surface concentration n at a constant value during the course of the reaction. A unimolecular constant was not obtained under these conditions, but on applying the integrated form of the Arrhenius equation

$$\frac{dx}{dt} = k\,\frac{(a-x)}{x}, \tag{5}$$

a constant value for the reaction velocity coefficient resulted, suggesting that under these conditions inhibition of the reaction results by adsorption from the solution of the product, the ionized hydroxy acid.

In bimolecular reactions it has been admitted that colliding molecules having the energy necessary for activation do not necessarily decompose unless suitably oriented. The alteration in the reaction velocity constant with change in the molecular area of the lactone is depicted in fig. 6. At 25° C. and under low compression γ-stearolactone films are partially expanded, and in this state the inclination of the polar groups will be altered as compared to the condensed films. The average value of k_2 (litres/gm. mol./min.) was $8 \cdot 4 \times 10^{-2}$ for condensed films, in which A varied from 24·5 to 29·8 A.^{2}. When the molecular area exceeded the limiting value for the condensed state (30 A.^{2}), and was altered from 33·1 to 42·3 A.^{2}, the reaction velocity coefficient k_2 increased to $1 \cdot 23 \times 10^{-1}$. This clearly demonstrates the importance of the orientation of the reactive portion of a molecule as a factor in determining the velocity.

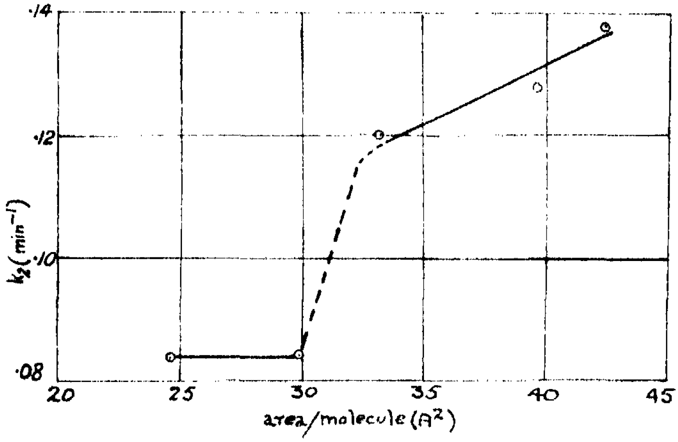


FIG. 6.—Hydrolysis on N . NaOH ; $t = 25°$ C.

The Kinetics of the Reaction.

The expression for the velocity of the reaction under consideration at a given concentration of reactant may be written

$$v = k_{\text{OH}}(\overline{\text{OH}}) + k_{\text{Na}^+}(\text{Na}^+) + k_{\text{W}}(\text{H}_2\text{O}). \tag{6}$$

Some experiments of Henry* and of Holmberg† on the hydrolysis of butyro- and valero-lactone have shown cation catalysis to be absent. Further, on a neutral buffer there is no detectable spontaneous reaction, and hence the above equation reduces to

$$v = k_{\text{OH}^-}(\text{OH}^-), \tag{7}$$

where k_{OH^-} is the catalytic coefficient of the hydroxyl ion.

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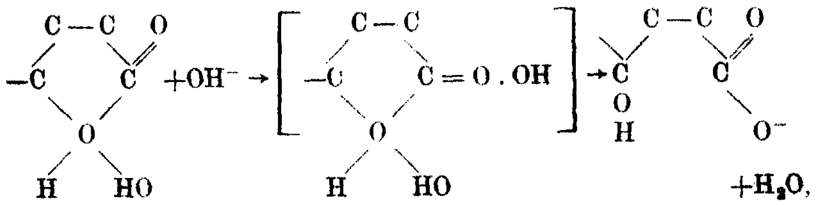
* 'Z. phys. Chem.,' vol. 10, p. 96 (1892).

† 'Z. phys. Chem.,' vol. 80, p. 587 (1912).

If we now assume the lactone hydrate and hydroxyl ion to react to form a critical complex which decomposes into the products of reaction, thus



then the measurable reaction is the rate of formation of the complex and the velocity equation may be written

$$v = k_{\mathrm{OH}} \,.\, (\mathrm{OH}) \,.\, (\mathrm{A}) \,.\, \frac{f\mathrm{A}\,.\,f\mathrm{OH}^-}{f(\mathrm{A}\,.\mathrm{OH})^-}\,, \tag{8}$$

where (A) is the lactone concentration and $f\mathrm{A}\,.\,f\mathrm{OH}'$, $f\mathrm{A}\,.\,\mathrm{OH}'$ the respective activity coefficients.

Since the activity coefficient depends on the ion type $f\mathrm{OH}^- / f(\mathrm{A}\,.\,\mathrm{OH})^-$ may be taken as unity and the expression becomes

$$v = k_{\mathrm{OH}} \,.\, (\mathrm{OH}) \,.\, (\mathrm{A}) \,.\, f\mathrm{A}. \tag{9}$$

In this type of interface reaction $f\mathrm{A} = f\mathrm{A}$ (solid) = unity, and the reaction velocity is directly proportional to the product of the concentration of the reactants as found experimentally.

In a reaction proceeding at a measurable speed the number of effective collisions is equal to the total number multiplied by the probability for a pair of molecules having the required energy and may be expressed by

$$v = se^{-\mathrm{E/RT}}. \tag{10}$$

Considering the hydrolysis of a stearolactone film on a normal solution of NaOH the number of molecules reacting per second per unit area may be obtained from the equation

$$v = k_2 \,.\, n_{\mathrm{A}}, \tag{11}$$

where n_{A} is the number of lactone molecules per square centimetre and k_2 the velocity constant expressed in sec.$^{-1}$. Inserting the value of k_2 found at 25° C. and putting $n_{\mathrm{A}} = 4 \times 10^{14}$ we find

$$v = 1{\cdot}405 \times 10^{-3} \,.\, 4{\cdot}0 \times 10^{14}$$
$$= 5{\cdot}61 \times 10^{11} \text{ molecules per second.}$$

The total number of collisions occurring at unit surface per second (s) may be evaluated by means of equation (10). Substituting the above value of v, and the experimentally determined value of E, we find for a temperature of 25° C.

$$\kappa = 5\cdot61 \times 10^{11}\, e^{-\frac{12.500}{596}}.$$
$$= 8\cdot0 \times 10^{20}.$$

It is possible from statistical considerations of the conditions existing at a solid-liquid interface as described by Langmuir* and by Butler† to evaluate v and s independently. If we consider a volume of solution at the film-interface equal in thickness to the mean free path of the solute molecules, the total number of hydroxyl ions reaching unit surface per second is given by

$$N_0 = N_S \sqrt{\frac{RT}{2\pi M}}, \qquad (12)$$

where

$R = 8\cdot3 \times 10^6$

M = molecular weight

T = absolute temperature

N_S = number of solute molecules per cubic centimetre.

Placing $M = 17$, $T = 298$, and $N_S = 6\cdot06 \times 10^{20}$, the following value is obtained for the total number of collisions per unit surface per second

$$N_0 = 9\cdot20 \times 10^{24}.$$

Now the expression for the number of hydroxyl ions arriving at the surface with kinetic energy E is

$$N'_0 = N_0\, e^{-\frac{E}{RT}} \qquad (13)$$

whence

$$N'_0 = 9\cdot20 \times 10^{24} \times e^{-\frac{12,500}{596}}$$
$$= 6\cdot45 \times 10^{15}.$$

If it is assumed that every collision between a hydroxyl ion with energy of activation E and a lactone ring results in a chemical reaction, then N'_0 should be equal to v. A comparison of the calculated and observed rates of reaction reveals a serious discrepancy for $v/N'_0 = 8\cdot2 \times 10^{-5}$. Moelwyn-Hughes‡ has shown that the observed and calculated reaction velocity coefficients for the alkaline hydrolysis of esters differ by the above value and the same thing is true for the hydrolysis of the stearolactone molecule by the alcoholate ion.

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* 'J. Amer. Chem. Soc.,' vol. 35, p. 105 (1913).

† 'Trans. Faraday Soc.,' vol. 19, p. 659 (1924).

‡ 'Phil. Mag.,' vol. 14, p. 112 (1932).

An attempt has been made by the above author to account for the discrepancy by assuming that in catalytic reactions between a neutral molecule and an ion in aqueous solution collisions between solute and solvent molecules must be considered. Since in this case the collision frequency is proportional to the viscosity of the solvent, η, it diminishes rapidly with an increase in temperature. Thus the true energy of activation of the reaction E^1 differs from that given by the Arrhenius equation and may be obtained by plotting the value of $\log k/\eta$ against $1/T$, fig. 4, curve *b*.

The value of E^1 *found by this procedure* was 17,100 calories per gram molecule. Hence the number of active collisions is given by

$$\begin{aligned} N'_0 &= N_0\, e^{-\frac{E^1}{RT}} \\ &= 9 \cdot 20 \times 10^{24} \times 2 \cdot 95 \times 10^{-13} \\ &= 2 \cdot 72 \times 10^{12}, \end{aligned} \tag{14}$$

and the ratio of v to N'_0 is reduced from $8 \cdot 20 \times 10^{-5}$ to $0 \cdot 21$ which is not an unreasonable agreement when one considers the observed effect of orientation on the reaction velocity coefficient.

It is possible to obtain information concerning the nature of the diffuse layer which exists beneath the film with the aid of expression (12) and the Fick diffusion equation

$$\frac{dx}{dt} = D \frac{c}{v} \cdot \frac{1}{\delta}, \tag{15}$$

where dx/dt is the number of gram mols of OH ion striking unit surface per second as deduced from (12),

D = diffusion coefficient per unit area per second under unit concentration gradient,

c/v = concentration in gram molecules per litre, and

δ = thickness of the diffuse layer.

Considering a normal solution of NaOH at 25° C. and substituting the values $D = 1 \cdot 73 \times 10^{-5}$ cm.²/sec., $c/v = 1 \cdot 0 \times 10^{-3}$, and $dx/dt = 15 \cdot 2$ gm. mols. per sec., we obtain

$$\begin{aligned} \delta &= \frac{1 \cdot 73 \times 10^{-8}}{15 \cdot 2} \\ &= 1 \cdot 14 \times 10^{-9} \text{ cm.} \end{aligned}$$

This value of δ is of the same order of magnitude as the calculated thickness of the Helmholtz double layer at the surface of a solution containing an ionized solute. The result is significant, for it indicates equivalence of concentration of the solute immediately beneath the film and in the bulk phase, which is of importance in the kinetic interpretation of surface reactions.

Summary.

(1) Films of γ-hydroxystearic acid and γ-stearolactone have been examined by the surface potential and surface pressure methods.

(2) From the behaviour of the electric moment of the hydroxy acid towards compression and temperature it is seen that the $>$CHOH may be removed from the surface when under compression.

(3) The surface potential equilibrium spreading values indicated the formation of complexes formed between lactone and substrate.

(4) The kinetics of the hydrolysis of γ-stearolactone have been studied and shown to be amenable to treatment by the kinetic theory applied to solutions.

On the Interaction between several Species of Hosts and Parasites.

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(Communicated by J. B. S. Haldane, F.R.S.—Received April 19, 1933.)

The problem of formulating mathematically the interaction between one species of Host and one species of Parasite has been investigated recently* by methods intended to be adequately comprehensive. Earlier investigations of this problem have been given by Lotka† and Volterra,‡ but both of these may be considered to be somewhat unsatisfactory on account of their neglect of the influence of the age-distribution on the interaction.

The more comprehensive theory in which the age-distributions are taken into consideration, may evidently be used to examine whether their neglect by Lotka and Volterra can be justified. It is not, however, proposed to do this here, particularly as it appears* that Volterra's formulation is not wholly self-consistent.

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* Bailey, 'Quart. J. Maths.,' vol. 2, p. 68 (1931).

† 'Wash. Acad. Sci.,' vol. 13, p. 152 (1923).

‡ 'Rend. Acc. Lincei.,' vol. 5, p. 3 (1927).

The more general problem involving several species of hosts and parasites may be investigated by similar methods which lead to a fundamental system of equations.

The following notation will be used:

A lower index refers to a particular host-species and an upper index to a particular parasite-species. Also for brevity the animals of the pth series will be termed p-animals.

Specified Quantities.

ξ, η the age of an animal,

$\phi(\xi)$ the probability that in unit time an animal of age ξ dies from environmental causes,

$\chi_q(\xi)$ the probability that in unit time a q-host of age ξ give birth to a new host,

$\gamma_q^p(\xi)$ the probability that a q-host of age ξ be in a condition to interact with the p-parasites,

$v_q^p(\eta)$ the effective velocity, areal or volumetric, of p-parasites of age η, in regard to their ability to find (and attack) q-hosts,†

l_q^p the number of eggs laid by a p-parasite in a q-host.

Derived Quantities.

$f(\xi) = \exp \int_0^{\xi} -\phi(x)\,dx$ is the probability at birth that, in the absence of parasites, an animal will survive environmental causes of death till the age ξ,

$k_q(\xi) = \chi_q(\xi) f_q(\xi)$ is the probability at its birth that a q-host, when aged ξ, will give birth to one new host per unit time,

$g_q^p(\xi) = \gamma_q^p(\xi) f_q(\xi)$,

$j_q^p(\eta) = v_q^p(\eta) f^p(\eta)$.

Unknown Quantities.

$N(t)$ density at time t, of all the animals of a given species,

$M_q^p(t)$ density at time t of those q-hosts which are in a condition to interact with p-parasites,

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* Bailey, *loc. cit.*, p. 76.

† In the interval of time dt n p-parasites of the age η searching among q-hosts of interaction probability γ and of density N per unit area, will attack a number proportional to $n\gamma N\,dt$. This introduces a factor of proportionability v_q^p which necessarily has the dimensions of an areal (or volumetric) velocity and is also a function of η.

$W_q^p(t)$ effective velocity at time t of the whole of the p-parasites in regard to their finding q-hosts,

$B(t)$ birth rate at time t of animals of a given species per unit area,

$A(t, \xi)$ age-distribution function at time t.

In connection with this scheme of notation the following points may be noted.

The effects of seasonal variations in the animals' properties can be included in the theory merely by treating the specified functions ϕ, χ, γ, v as functions of t as well as of ξ or η.

The sex-ratios are assumed to remain constant, and the densities and properties of the animals include both sexes. Without reducing the generality of the results in any way this serves to keep the formulæ from being encumbered with additional multiplicative constants.

The age of a parasite is taken to be the time which has elapsed since it was laid as an egg.

The individuals of each host-species are regarded as moving at rates independent of their ages in order to keep the formulæ simpler than they would be if these rates varied with their ages. As suggested in the special theory* the effect of the hosts possessing motions can be derived by methods analogous to those used by Maxwell† in 1860 in connection with the dynamical theory of gases. It is not difficult to generalize our theory in this way to include host-velocities variable with age,‡ but for the present it appears desirable to postpone such a generalization until the equations of the simpler theory are established and some progress made with their discussion.

The density is supposed to be uniform throughout the space in which the animals interact.

The way is now clear for deriving these equations, it being noted that the reasoning is always referred to unit area.

Considering first the hosts, from the definition we immediately deduce the equations

$$\int_0^\infty A_q(t, \xi)\, d\xi = 1, \qquad (q = 1, 2, 3, \ldots, Q). \tag{1}$$

Let n_0 be a number of q-hosts which are born all nearly at the same time τ, and let $n(x)$ denote the number of these which survive to the age x.

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* Bailey, *loc. cit.*, p. 70, footnote.

† "Collected Papers," vol. 1, p. 387.

‡ It would amount to replacing $v_q^p(\eta)$ by $v_q^p(\eta, \xi)$.

In the interval of time dx they encounter parasites of the different species with the result that the number of interactions is

$$\Sigma^p \mathrm{W}_q^{\,p}(\tau + x)\,\gamma_q^{\,p}(x)\,n(x)\,dx\,;$$

also the number of deaths is $\phi_q(x)\,n(x)\,dx$.

Therefore

$$-dn(x) = \{\phi_q(x) + \Sigma^p \mathrm{W}_q^{\,p}(\tau + x)\,\gamma_q^{\,p}(x)\}\,n(x)\,dx,$$

and so

$$n(\xi) = n_0 f_q(\xi) \exp \int_0^{\xi} - \Sigma^p \mathrm{W}_q^{\,p}(\tau + x)\,\gamma_q^{\,p}(x)\,dx.$$

At time t the $\mathrm{N}_q(t)\,\mathrm{A}_q(t, \xi)\,d\xi$ hosts of ages ξ to $\xi + d\xi$ are the survivors of the $\mathrm{B}_q(t - \xi)\,d\xi$ hosts born in the interval $t - \xi$ to $t - \xi + d\xi$. So in the last equation we may set $\tau = t - \xi$, $n_0 = \mathrm{B}_q(t - \xi)\,d\xi$ and

$$n(\xi) = \mathrm{N}_q(t)\,\mathrm{A}_q(t, \xi)\,d\xi,$$

and thus obtain

$$\mathrm{N}_q(t)\,\mathrm{A}_q(t, \xi) = \mathrm{B}_q(t - \xi) f_q(\xi) \exp \int_0^{\xi} - \Sigma^p \mathrm{W}_q^{\,p}(t - \xi + x)\,\gamma_q^{\,p}(x)\,dx. \quad (2)$$

The birth rate from q-hosts of ages ξ to $\xi + d\xi$ is $\mathrm{N}_q(t)\,\mathrm{A}_q(t, \xi)\,\chi_q(\xi)\,d\xi$, so the total birth rate is

$$\mathrm{B}_q(t) = \mathrm{N}_q(t) \int_0^{\infty} \mathrm{A}_q(t, \xi)\,\chi_q(\xi)\,d\xi. \quad (3)$$

Considering now the p-parasites we find from the definition that

$$\int_0^{\infty} \mathrm{A}^p(t, \eta)\,d\eta = 1, \qquad (p = 1, 2, 3, \ldots, \mathrm{P}). \quad (4)$$

By means of reasoning similar to that which yielded (2) we get

$$\mathrm{N}^p(t)\,\mathrm{A}^p(t, \eta) = \mathrm{B}^p(t - \eta) f^p(\eta). \quad (5)$$

The $\mathrm{N}^p(t)\,\mathrm{A}^p(t, \eta)\,d\eta$ parasites of ages η to $\eta + d\eta$ have an effective velocity $\mathrm{N}^p(t)\,\mathrm{A}^p(t, \eta)\,v_q^{\,p}(\eta)\,d\eta$ with respect to the q-hosts. Therefore

$$\mathrm{W}_q^{\,p}(t) = \mathrm{N}^p(t) \int_0^{\infty} \mathrm{A}^p(t, \eta)\,v_q^{\,p}(\eta)\,d\eta. \quad (6)$$

Substituting from (2) in (3) we obtain

$$\mathrm{B}_q(t) = \int_0^{\infty} \mathrm{B}_q(t - \xi)\,k_q(\xi) \exp \left\{ \int_0^{\xi} - \Sigma^p \mathrm{W}_q^{\,p}(t - \xi + x)\,\gamma_q(x)\,dx \right\} d\xi. \quad (7)$$

Multiplying (2) by $\gamma_q^p(\xi)$ and integrating we find

$$M_q^p(t) = \int_0^\infty B_q(t-\xi)\, g_q^p(\xi) \exp\left\{\int_0^\xi - \Sigma^p W_q^p(t-\xi+x)\, \gamma_q^p(x)\, dx\right\} d\xi. \tag{8}$$

Substituting from (5) in (6) gives

$$W_q^p(t) = \int_0^\infty B^p(t-\eta)\, j_q^p(\eta)\, d\eta. \tag{9}$$

The birth-rate of p-parasites is evidently given by

$$B^p(t) = \Sigma_q l_q^p M_q^p(t)\, W_q^p(t). \tag{10}$$

There are clearly as many equations in the system (7)–(10) as there are unknown functions.

When the values of B_q and B^p are given for all moments during a time preceding $t = 0$ which exceeds the longest possible age of any of the animals, this system of equations determines the quantities $M_q^p(t)$, $W_q^p(t)$, $B_q(t)$, $B^p(t)$ for any later time t.

We can then determine $N_q(t)$ and $A_q(t, \xi)$ from (1) and (2), and $N^p(t)$ and $A^p(t, \eta)$ from (4) and (5).

We now enquire whether a steady state is possible, *i.e.*, whether solutions of (7)–(10) can be found which are independent of the time t. If m_q^p, w_q^p, b_q, b^p are the steady values of M_q^p, W_q^p, B_q, B^p respectively, they must satisfy the following system of equations :—

$$1 = \int_0^\infty k_q(\xi) \exp\left\{- \Sigma^p w_q^p \int_0^\xi \gamma_q^p(x)\, dx\right\} d\xi, \tag{7.1}$$

$$m_q^p = b_q \int_0^\infty g_q^p(\xi) \exp\left\{- \Sigma^p w_q^p \int_0^\xi \gamma_q^p(x)\, dx\right\} d\xi, \tag{8.1}$$

$$w_q^p = b^p \int_0^\infty j_q^p(\eta)\, d\eta. \tag{9.1}$$

$$b^p = \Sigma_q l_q^p m_q^p w_q^p. \tag{10.1}$$

There are as many equations in this system as unknown quantities. Nevertheless, it will be seen that when the number P of parasite-species is less than the number Q of host-species the quantities b^p are over-determined. This is because when the expressions for w_q^p in (9.1) are substituted in (7.1) there results Q equations in the P unknowns b^p.

Hence we conclude that a steady state is in general not even theoretically possible when there are less parasite-species than host-species.

When $P = Q$ a steady state, in general, can exist (provided the densities are positive).

When $P > Q$ the possibility of a steady state depends on the properties of the interacting species. But the discussion of this question will be given in another publication.

To each species, there can be assigned an upper limit T for the age of an individual, and so the upper limits ∞ in the integrals in (7), (8) and (9) may be replaced respectively by T_q, T_q, and T^p since

$$f_q(\xi) = 0, \text{ when } \xi > T_q,$$
$$f^p(\eta) = 0, \text{ when } \eta > T^p.$$

2. *A Simplification.*

The equations (7) and (8) are difficult to manipulate as they stand, but they become considerably simpler when the probability of interaction of any host-species with any parasite-species is independent of the ages of the host individuals, that is, when

$$\gamma_q{}^p(\xi) = c_q{}^p, \tag{11}$$

a constant for each pair of values of p and q.

For if we set

$$\left.\begin{aligned} Z_q{}^p(t) &= c_q{}^p \int_0^t W_q{}^p(\tau)\,d\tau \\ \text{i.e.,}\quad c_q{}^p W_q{}^p(t) &= Z_q{}^{p\prime}(t) \end{aligned}\right\}, \tag{12}$$

then

$$\int_0^t -\Sigma^p\, W_q{}^p(t-\xi+x)\,\gamma_q{}^p(x)\,dx = \Sigma^p\{Z_q{}^p(t-\xi) - Z_q{}^p(t)\},$$

and so with the substitution

$$X_q(t) = B_q(t)\,e^{\Sigma^p Z_q{}^p(t)}, \tag{13}$$

(7) and (8) respectively become

$$X_q(t) = \int_0^{T_q} X_q(t-\xi)\,k_q(\xi)\,d\xi, \tag{14}$$

and

$$M_q{}^p(t)\,e^{\Sigma^p Z_q{}^p(t)} = \int_0^{T_q} X_q(t-\xi)\,g_q{}^p(\xi)\,d\xi. \tag{15}$$

Also (9) and (10) become

$$Z_q^{p\prime}(t) = c_q^p \int_0^{T^p} B^p(t-\eta)\, j_q^p(\eta)\, d\eta \tag{16}$$

$$B^p(t) = \Sigma_q (l_q^p / c_q^p)\, M_q^p(t)\, Z_q^{p\prime}(t). \tag{17}$$

For the steady state the equations (12)–(17) become

$$z_q^p = c_q^p w_q^p t \tag{12.1}$$

$$x_q = b_q\, e^{(\Sigma^p c_q^p w_q^p)\, t} \tag{13.1}$$

$$1 = \int_0^{T_q} e^{-(\Sigma^p c_q^p w_q^p)\,\xi}\, k_q(\xi)\, d\xi \tag{14.1}$$

$$m_q^p = b_q \int_0^{T_q} e^{-(\Sigma^p c_q^p w_q^p)\,\xi}\, g_q^p(\xi)\, d\xi \tag{15.1}$$

$$w_q^p = b^p \int_0^{T^p} j_q^p(\eta)\, d\eta \tag{16.1}$$

$$b^p = \Sigma_q\, l_q^p m_q^p w_q^p. \tag{17.1}$$

Equation (14) can be put in the operator form

$$\left\{1 - \int_0^{T_q} e^{-\xi D} k_q(\xi)\, d\xi\right\} X_q(t) = 0,$$

where D stands for d/dt, from which we see that its general primitive is

$$X_q(t) = \Sigma_r\, C_r\, e^{\alpha_r t}, \tag{18}$$

where the C_r's are arbitrary constants and the α_r's are the roots of this equation in α:

$$1 - \int_0^{T_q} e^{-\alpha\xi} k_q(\xi)\, d\xi = 0. \tag{19}$$

Since $k_q(\xi)$ is always positive in virtue of its definition, the equation (19) has only one real root, which, by comparison of (19) with (14.1), is evidently

$$\alpha_q = \Sigma^p c_q^p w_q^p.$$

Since the quantities X_q are real the coefficients C_r for conjugate roots α_r must be themselves conjugate numbers.

Writing

$$Y_q(t) = e^{-\alpha_q t} X_q(t) \tag{20}$$

we obtain from (14)

$${}_q(t) = \int_0^{T_q} Y_q(t-\xi)\, K_q(\xi)\, d\xi, \tag{21}$$

where

$$K_q(\xi) = k_q(\xi)\, e^{-a_q \xi} > 0,$$

for which by (14.1)

$$\int_0^{T_q} K_q(\xi)\, d\xi = 1. \tag{22}$$

The general solution of (21) is

$$Y_q(t) = C_q + \Sigma_r\, C_r\, e^{\theta_r t}, \tag{23}$$

where the θ_r's are the roots other than zero, of the equation

$$\int_0^{T_q} e^{-\theta\xi} K_q(\xi)\, d\xi = 1. \tag{24}$$

Since there can be only one real value of θ, namely, zero, which satisfies this, it is clear that the θ_r's are all complex.

We now investigate the sign of their real parts by setting

$$\theta = u + iv \qquad (u \text{ and } v \text{ real}),$$

in (24) and subtracting (22), so obtaining

$$\int_0^{T_q} (e^{-u\xi} \cos v\xi - 1)\, K_q(\xi)\, d\xi = 0.$$

Since $K_q(\xi) > 0$ and $\cos v\xi \leqslant 1$ this relation cannot be satisfied unless $e^{-u\xi} > 1$.

We thus conclude that u *is negative.*

Hence the terms in $\Sigma_r C_r e^{\theta_r t}$ represent damped oscillations, and so ultimately $Y_q(t) \rightarrow C_q$ as $t \rightarrow \infty$.

It is interesting to note that the only properties of the animals on which the vanishing terms depend are the breeding properties of the hosts.

It will be noticed that corresponding to the steady state we must have $Y_q = b_q$ in order to satisfy (13.1), *i.e.*, for the steady state $C_q = b_q$ and every $C_r = 0$.

We now proceed to obtain a system of equations with the B^p's as the only unknown functions.

Integrating (16) with respect to t from 0 to t, and remembering (12), therefore

$$Z_q^p(t) = \int_0^t dt \int_0^{1^p} B^p(t-\eta)\, i_q^p(\eta)\, d\eta,$$

where

$$i_q^p(\eta) = c_q^p j_q^p(\eta).$$

Eliminating the Z_q^p's and M_q^p's from (17) by means of this equation and (15) we obtain

$$\mathrm{B}^p(t) = \Sigma_q \Big[(l_q^p / c_q^p) \int_0^{\mathrm{T}^p} \mathrm{B}^p(t-\eta)\, i_q^p(\eta)\, d\eta \times e^{-\Sigma^s \int_0^t dt \int_0^{\mathrm{T}^s} \mathrm{B}^s(t-\theta)\, i_q^s(\theta)\, d\theta} \,.\, \int_0^{\mathrm{T}_q} \mathrm{X}_q(t-\xi)\, g_q^p(\xi)\, d\xi \Big]. \tag{25}$$

This is the required system of P equations in the P unknowns B^p.

As $t \to \infty$ this system tends to the following form

$$\mathrm{B}^p(t) = \Sigma_q \Big[(\mathrm{C}_q l_q^p m_q^p / c_q^p b_q) \int_0^{\mathrm{T}^p} \mathrm{B}^p(t-\eta)\, i_q^p(\eta)\, d\eta \times e^{-\Sigma^s \int_0^t dt \int_0^{\mathrm{T}^s} \beta^s(t-\theta)\, i_q^s(\theta)\, d\theta} \Big], \tag{25.1}$$

where

$$\beta^p(t) = \mathrm{B}^p(t) - b^p ;$$

this follows from the fact that $\mathrm{Y}_q \to \mathrm{C}_q$, (15.1) and (16.1).

When the values of all the B^p's during the respective intervals of time $t = -\mathrm{T}^p$ to $t = 0$ are specified the system (25) determines the functions $\mathrm{B}^p(t)$, and so by means of (16), (15), (13), (1) with (2) and (4) with (5) we can obtain the functions W_q^p, M_q^p, B_q, N_q and N^p respectively.

It will be noticed that in treating the birth rates B^p and B_q as the fundamental functions instead of N^p and N_q we secure in essence the additional advantage of simultaneously representing the four functions N^p, N_q, A^p and A_q.

Behaviour near the Steady State.—This may be investigated by treating all the β^p's as quantities of the first order of smallness. Also while the functions all remain near their steady values we must in (23) set $\mathrm{C}_q = b_q + c_q$ with c_q and all the C_r's of the first order of smallness.

Thus (25) becomes

$$b^p + \beta^p(t) = \Sigma_q \Big[(l_q^p / c_q^p) \int_0^{\mathrm{T}^p} (b^p + \beta^p(t-\eta))\, i_q^p(\eta)\, d\eta \times e^{-\Sigma^s \int_0^t dt \int_0^{\mathrm{T}^s} [b^s + \beta^s(t-\theta)]\, i_q^s(\theta)\, d\theta + a_q t} \times \int_0^{\mathrm{T}_q} \mathrm{Y}_q(t-\xi)\, e^{-a_q \xi} g_q^p(\xi)\, d\xi \Big],$$

with $\mathrm{Y}_q(t) = b_q + y_q(t)$, where $y_q(t) = c_q + \Sigma_r \mathrm{C}_r e^{s_r t}$ and is of the first order of smallness.

By (16.1)

$$\Sigma^s \int_0^t dt \int_0^{T^s} b^s i_q^s(\theta)\, d\theta = \alpha_q t,$$

and so, expanding the exponential we obtain

$$b^p + \beta^p(t) = \Sigma_q \Big[(l_q^p / c_q^p) \int_0^{T^p} (b^p + \beta^p(t-\eta))\, i_q^p(\eta)\, d\eta$$

$$\times \left\{1 - \Sigma^s \int_0^t dt \int_0^{T^s} \beta^s(t-\theta)\, i_q^s(\theta)\, d\theta + \dots\right\} \{m_q^p + \phi_q(t)\}\Big],$$

where

$$\phi_q(t) = \int_0^{T_q} y_q(t-\xi)\, e^{-\alpha_q \xi} g_q^p(\xi)\, d\xi,$$

and is also of the first order of smallness.

Multiplying out and neglecting quantities of higher order of smallness than the first we get

$$\beta^p(t) = \Sigma_q \Big[h_q^p \int_0^{T^p} \beta^p(t-\eta)\, i_q^p(\eta)\, d\eta$$

$$- k_q^p \Sigma^s \int_0^t dt \int_0^{T^s} \beta^s(t-\theta)\, i_q^s(\theta)\, d\theta + l_q^p w_q^p \phi_q(t)\Big],$$

where $h_q^p = l_q^p m_q^p / c_q^p$ and $k_q^p = l_q^p m_q^p w_q^p$.

Differentiating with respect to t then yields

$$\beta^{p\prime}(t) = \Sigma_q \Big[h_q^p \int_0^{T^p} \beta^{p\prime}(t-\eta)\, i_q^p(\eta)\, d\eta - k_q^p \Sigma^s \int_0^{T^s} \beta^s(t-\theta)\, i_q^s(\theta)\, d\theta + F^p(t), \tag{26}$$

where

$$F^p(t) = \Sigma_q l_q^p w_q^p \phi'_q(t).$$

On making the substitution $t - \eta = x$ this can be treated as a system of simultaneous linear integro-differential equations with $i_q^p(t-x)$ as the nuclei, but the following method avoids the necessity for recourse to a somewhat recondite subject.

Introducing the operators

$$O_q^p(D) \equiv \int_0^{T^p} e^{-\eta D} i_q^p(\eta)\, d\eta,$$

where $D \equiv d/dt$ we can write (26) in the form

$$D\{1 - \Sigma_q h_q^p O_q^p(D)\}\, \beta^p(t) + \Sigma_q k_q^p \Sigma^s O_q^s(D)\, \beta^s(t) = F^p(t), \tag{27}$$

where

$$\mathrm{F}^p(t) = \Sigma_q l_q{}^p w_q{}^p \, \Sigma_r \mathrm{C}_r \theta_r \int_0^{\mathrm{T}^q} e^{-(a_q+\theta_r)\xi} g_q{}^p(\xi)\, d\xi \,.\, e^{\theta_r t}.$$

This represents a system of P equations in the P unknowns β^p.

The general primitive, subject to conditions of convergence is

$$\beta^p(t) = \Sigma_r \mathrm{C}_r{}^p e^{\lambda_r t} + \mathrm{I}^p(t),$$

where the $\mathrm{C}_r{}^p$'s are arbitrary, the λ_r's are the roots of the eliminant of the system of P equations

$$\lambda\{1 - \Sigma_q h_q{}^p \mathrm{O}_q{}^p(\lambda)\} \mathrm{C}^p + \Sigma_q k_q{}^p \Sigma^s \mathrm{O}_q{}^s(\lambda) \mathrm{C}^s = 0, \tag{28}$$

when the C^p's are eliminated, and the functions $\mathrm{I}^p(t)$ are the particular integrals of (27).

Since each $\mathrm{F}^p(t)$ represents a system of damped oscillations so will each $\mathrm{I}^p(t)$.

Hence the ultimate behaviour near the steady state will always tend towards the special type represented by

$$\beta^p(t) = \Sigma_r \mathrm{C}_r{}^p e^{\lambda_r t}. \tag{29}$$

When there is only one host-species and only one parasite-species the eliminant of (28) takes the simple form

$$\lambda + \frac{k\mathrm{O}(\lambda)}{1 - h\mathrm{O}(\lambda)} = 0,$$

where

$$h\mathrm{O}(\lambda) = \int_0^{\mathrm{T}^p} e^{-\eta\lambda} j(\eta)\, d\eta \Big/ \int_0^{\mathrm{T}^p} j(\eta)\, d\eta.$$

Thus the equation in λ may be written as

$$\lambda + c\, \frac{\int_0^{\mathrm{T}^p} e^{-\eta\lambda} j(\eta)\, d\eta}{\int_0^{\mathrm{T}^p} (1 - e^{-\eta\lambda}) j(\eta)\, d\eta} = 0, \tag{30}$$

where

$$c = k/h.$$

Since the two terms on the left-hand side always have the same sign when λ is real, it follows that this equation has no real roots.

From the definition of the function $j(\eta)$ it is clear that as η ranges from 0 to T^p this quantity increases from zero to a maximum value and then diminishes back to zero, always remaining positive.

Following Prony* we may represent $j(\eta)$ by means of a sum of exponentials. For a simple treatment we can adopt as a first approximation to this property of the parasites the following representation:

$$j(\eta) = a\,e^{-\mu\eta} - a\,e^{-\nu\eta},$$

where $a > 0$, $\nu > \mu > 0$, and $T^p \rightarrow \infty$.

Now

$$\int_0^\infty e^{-\eta\lambda} j^p(\eta)\,d\eta = \frac{a}{\lambda+\mu} - \frac{a}{\lambda+\nu} = \frac{a(\nu-\mu)}{(\lambda+\mu)(\lambda+\nu)},$$

provided that the real part of $\lambda+\mu$ is positive, which will be verified later. So (30) becomes

$$\lambda + c\,\frac{a\mu\nu}{\lambda^2+\lambda(\mu+\nu)} = 0,$$

i.e.,

$$\lambda^2 + \frac{d}{\lambda+f} = 0,$$

where d and f are positive.

Let $\lambda = u + iv$ where u and v are real. Therefore

$$u^2 - v^2 + 2uvi + \frac{d\,((u+f)-vi)}{(u+f)^2+v^2} = 0.$$

From the imaginary part we get

$$2uv = v\,\frac{d}{(u+f)^2+v^2}.$$

But $v \neq 0$, since λ has no real values. Therefore *u is positive.*

This result is true for any root. We thus verify the supposition that $\lambda+\mu$ has a positive real part.

Hence in this case the terms in (29) represent an *increasing* oscillation.

Hence the function β^p and so the functions B^p, B_q, N^p N_q, are oscillating functions of time whose amplitudes of oscillation increase with time. This means that the *steady state is unstable*, and so it cannot be ultimately converged upon.

The problem of extending these methods to the situation in which there are several species remains to be solved.

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* See Whittaker and Robinson's "Calculus of Observations," p. 369.

3. *General Discussion.*

The only other detailed investigation of the general problem of interaction of species of animals appears to be that due to Volterra.*

His formulation of the fundamental equations may, however, be criticized on several grounds, and such a criticism will be given in the future in a publication on animal populations written jointly with Dr. A. J. Nicholson. It suffices here to mention that Volterra's theory takes no account of the effect of the age-distribution of the animals.

The theory given here can be generalized further to include hyperparasites of all ranks. We call animal-species of the nth rank those which prey upon species of the $(n - 1)$th rank and which in turn are preyed upon by species of the $(n + 1)$th rank. If the index-symbols p and q in equations (1) to (6) are replaced respectively by p_{n+1} and p_n, where n runs through a series of consecutive integers, the resulting equations describe the interaction completely. There is, however, only one group of equations like (3), namely, that for the species of lowest rank, and one group like (5), namely, that for the species of highest rank.

A system of fundamental equations analogous to the system (7)-(10) can thus be obtained.

This formulation is fairly simple, but any discussion of the general character of the solutions must necessarily be postponed until further progress has been made with the less general problem involving only two ranks of species.

The principal questions requiring answers relate to the variations of the densities from the steady values, and in particular to the possible increase or decrease with time of such variations when they are oscillatory.

A promising point of attack is offered by the further study of the system of equations (25).

It may be mentioned that I have been able to obtain a complete solution of the problem of the behaviour near the steady state in a special case of non-continuous interaction† between one host-species and one parasite-species, which shows that their densities also oscillate about the steady values with amplitudes which *increase* with time.

Thus it is probable that this behaviour is true generally.

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* "Théorie Mathématique de la Lutte pour la Vie." (Gauthier Villars, 1931.) Edited by M. Brelot. Lotka has also discussed the general problem in his admirable book "Elements of Physical Biology" (Williams and Wilkins Co., 1925)) but the treatment is broad and hardly any definite conclusions emerge.

† 'Proc. Camb. Phil. Soc.,' vol. 29, p. 1187 (1933).

In conclusion I wish to express my indebtedness to Dr. A. J. Nicholson and Mr. R. C. B. Lane for their helpful criticisms.

Summary.

The problem of formulating mathematically the interaction between several species of hosts and parasites is investigated, and *the fundamental equations which serve to determine the population densities and the age-distributions in these populations at any time are derived.*

From these are deduced the equations which determine the population densities, etc., in the steady state, when such a state is possible. It is shown that *a steady state is impossible when the number of parasite-species is less than the number of host-species.*

The discussion is much simplified when restricted to those host-species whose individuals have probabilities of interaction which are independent of their ages. The behaviour near the steady state is then shown to depend on a certain system of simultaneous linear integro-differential equations. By means of these it is deduced that *when only two species interact the steady state is unstable* to a first approximation. Reasons are given for regarding this result as being more generally true.

The extension of the theory which is needed to include hyperparasites is also indicated.

The Kinetics of Electrode Processes.—Part III. *The Behaviour of Platinum and Gold Electrodes in Sulphuric Acid and Alkaline Solutions containing Oxygen.*

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(Communicated by J. Kendall, F.R.S.—Received May 12, 1933.)

The first paper of this series* contained a general survey of the reactions of hydrogen and oxygen at platinum electrodes in dilute sulphuric acid solutions. We have now investigated in greater detail some of the phenomena which were observed, using mainly small polarizing currents, by means of which they can be more conveniently studied, and extending the scope of the experiments to other metals and solutions. In this paper an account is given of further experiments on platinum electrodes in the presence of oxygen, and of an investigation of the behaviour of gold electrodes in sulphuric acid and alkaline solutions. The experimental arrangements were similar to those previously described.

Platinum Electrodes in Oxygen Saturated Solutions.

Cathodic Depolarization by Oxygen.—If a platinum electrode in sulphuric acid is anodically polarized until oxygen is liberated and the current is then reversed, a marked depolarization process occurs at about $\varepsilon_H = +0 \cdot 05$. Bowden's† suggestion that this process is the reduction of a platinum oxide was shown in Part I to be untenable, because the length of the arrest of the potential is much reduced even by gentle stirring. The depolarization must be caused by some substance which is formed in the solution during the anodic polarization. Since it appeared that ordinary oxygen in the solution is not very active as a cathodic depolarizer in this region, it was suggested that the discharged oxygen remained for a time in a particularly active condition, but tests of the solution failed to reveal any enhanced oxidizing power.

When a platinum electrode is cathodically polarized in sulphuric acid containing oxygen, the cathodic depolarization which can be ascribed to the reduction of oxygen is variable in amount and in the potential at which it occurs. It has now been found that if the electrode is previously polarized for a short time to the point at which oxygen is formed, well defined and reproducible cathodic depolarization curves are obtained. Some of the curves obtained in this way are shown in fig. 1(*a*). The electrode had an apparent area of 4 cm.². Before each curve the electrode was polarized anodically with

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* 'Proc. Roy. Soc.,' A, vol. 137, p. 604 (1932); cited later as I.

† *Ibid.*, A, vol. 125, p. 446 (1929).

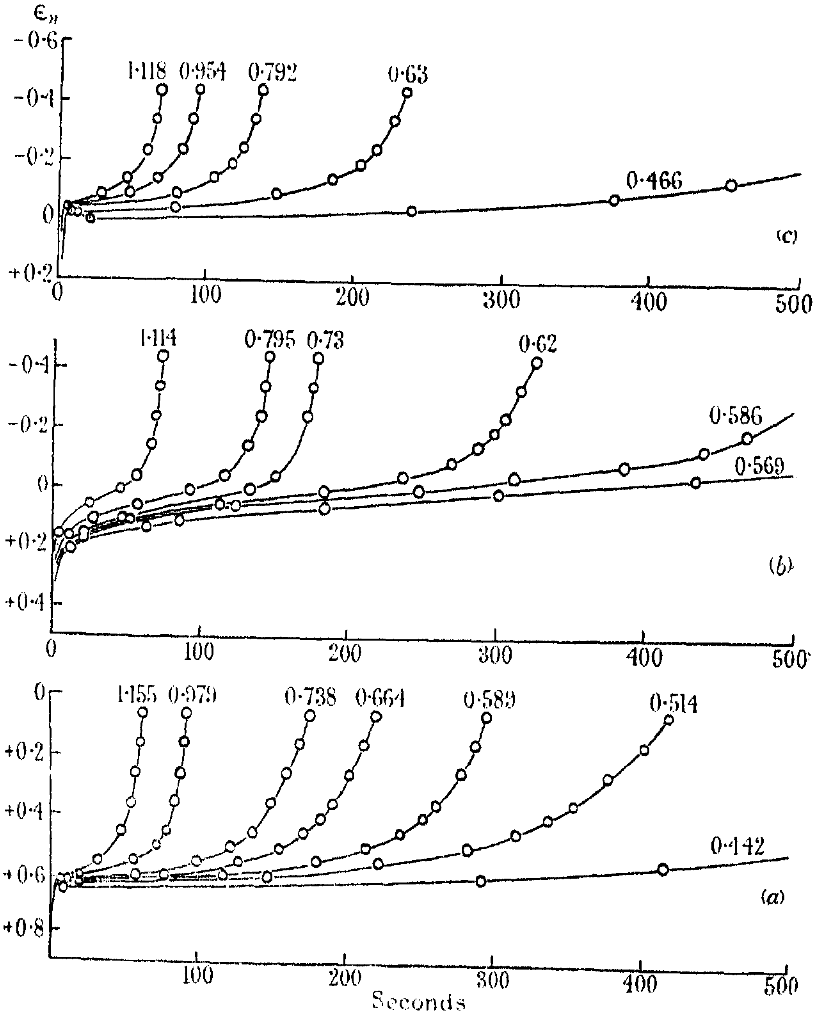

FIG. 1.—Cathodic depolarization by oxygen at platinum electrodes which have previously been polarized anodically for a short time. Currents in milliamperes. (*a*) M/10 H_2SO_4; (*b*) p_H 8 solution; (*c*) N/5 NaOH.

$1 \cdot 5 \times 10^{-3}$ amps. for 15 seconds, and the solution was then stirred by a stream of oxygen for 5 minutes. The oxygen produced in the anodic polarization has no appreciable influence on the length of the cathodic curve, for apart from the stirring, the amount liberated is insignificant compared with the amount of cathodic polarization. The cathodic current was stopped when the potential reached $\varepsilon_H = +0 \cdot 05$, to avoid the formation of hydrogen in the solution.

Beans and Hammett* have shown that while in acid solutions traces of oxygen have no appreciable effect on the reversible hydrogen potential at platinized electrodes, its electromotive activity is much greater in alkaline solutions. On examining the depolarization produced by oxygen in N/5 sodium hydroxide, we found that reproducible cathodic curves were obtained without the preliminary anodic treatment, if the solution was well stirred between successive experiments. Almost identical curves were obtained when the preliminary anodic polarization was carried out, fig. 1 (*c*). In a buffer solution of $p_H = 8$ (0·05 M KH_2PO_4; 0·047 N NaOH) a considerable amount of cathodic depolarization occurred at electrodes which had not been anodically polarized, but the curves were somewhat unreproducible. Very reproducible curves were obtained after a short anodic polarization, fig. 1 (*b*).

These curves have characteristics similar to those obtained for cathodic depolarization by solutions of methylene blue and quinhydrone.† In these cases it has been shown that as a result of the gradual depletion of the depolarizer in the vicinity of the electrode, the length of the depolarization curve to the final rapid rise of potential is, for times greater than about 100 seconds, in accordance with the equation

$$it_\infty = \alpha + \beta t_\infty, \tag{1}$$

where t_∞ is the transition time, *i.e.*, the time taken to reach an arbitrarily chosen potential on the rapidly rising part of the curve and i the current.

Table I gives the transition times with various currents for electrodes which had the previous anodic treatment.

The equation (1) holds for transition times above about 80 seconds. The slope β, which has been shown to be approximately proportional to the concentration of the depolarizer is practically the same in the sodium hydroxide and sulphuric acid solutions, but is appreciably greater in the p_H 8 solution. This is probably due to the somewhat greater solubility of oxygen in the buffer solution. It is evident that the cathodic depolarization in this region which was previously observed at electrodes which have been the anode both in oxygen and hydrogen saturated solutions must be ascribed to a high local concentration of oxygen.

* 'J. Amer. Chem. Soc.,' vol. 47, p. 1215 (1925).

† 'Proc. Roy. Soc.,' A, vol. 139, p. 406 (1933).

Anodic Polarization.—After the cathodic depolarization process represented in fig. 1, a considerable amount of anodic polarization is necessary before the potential reaches a steady value. This was previously investigated with large currents. Fig. 2 (*a*) shows the anodic curves of a 1 cm.^{2} electrode in sulphuric

Table I.—Transition Times for Oxygen Depolarization at Platinum Electrodes. i, amps. $\times 10^{-3}$; t_∞, seconds ; it_∞, Coulombs $\times 10^{-3}$.

Sulphuric acid. $\beta = 3 \cdot 6 \times 10^{-4}$.			p_H 8 solution. $\beta = 6 \cdot 0 \times 10^{-4}$.			Sodium hydroxide. $\beta = 3 \cdot 7 \times 10^{-4}$.		
i.	t_∞.	it_∞.	i.	t_∞.	it_∞.	i.	t_∞.	it_∞.
1·155	61	70	1·114	69	77	1·118	67	75
0·979	91	89	0·795	140	111	0·954	90	86
0·738	169	125	0·730	171	125	0·972	133	105
0·644	213	141	0·620	284	176	0·630	227	143
0·589	288	170	0·586	494	289	0·466	557	260
0·514	400	206	0·569	1035	589			
0·442	802	354						

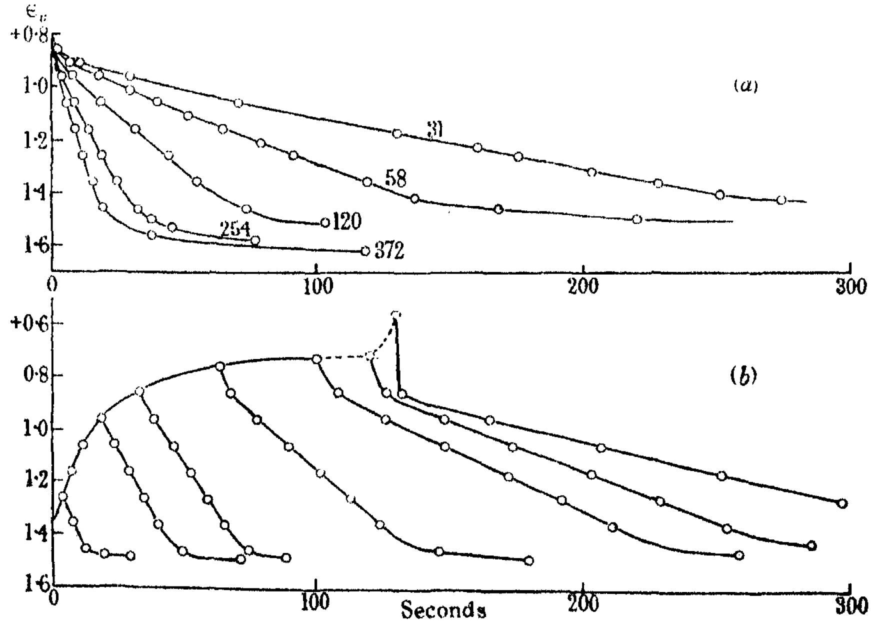

Fig. 2.—(*a*) Anodic curves of platinum in sulphuric acid (currents $\times 10^{-7}$ amps.). (*b*) Anodic curves of platinum with 31·4 $\times 10^{-7}$ amps. after cathodic polarization to various potentials. (The last two curves, initial voltages +0·71 and +0·56, are displaced horizontally relative to the others. The curve for the initial voltage +0·36 is shown in (*a*).)

acid which has been polarized cathodically to $+0\cdot36$ before each curve. The fall of potential is nearly linear with the time and the quantity of electricity required to cause the potential to change by $0\cdot1$ volt increases only slowly as the current is decreased. In Table II is given the number of coulombs required for $0\cdot1$ volt between $+1\cdot06$ and $+1\cdot26$ volts.

Table II.

Current	31·4	58	120	254	372×10^{-7} amps.
Coulombs for 0·1 volt	1·63	1·48	1·56	1·27	$1\cdot12 \times 10^{-4}$

These quantities are much greater than corresponds with the capacity of the double layer, for when the voltage was allowed to decay and a small anodic current was re-started only $1\cdot0 \times 10^{-5}$ coulombs were required for a change of $0\cdot1$ volt, and the potential rose initially on cathodic polarization at the same rate. Similar curves at more negative potentials were obtained in N/10 barium hydroxide. The total passage of current during the linear parts of the curves, about $0\cdot6$ volts, is 9×10^{-4} coulombs. If the true area of the electrode is taken as three times its apparent area (*see* I) it may be estimated that there are $4\cdot8 \times 10^{15}$ atoms of platinum at the surface, and the quantity of electricity required to form a layer of oxygen atoms spaced one to each platinum is 16×10^{-4} coulombs, which corresponds fairly closely with the amount observed. It may therefore be supposed that in the anodic polarization an approximately complete layer of adsorbed oxygen is formed.

It has been suggested (I) that on account of the energy of adsorption the formation of adsorbed oxygen atoms would require a smaller expenditure of energy and would therefore occur at a more negative potential than is required for their continuous formation in the solution. This hypothesis would require that the ions should already be in or near the adsorption positions of the subsequently formed atoms. If the discharge of the ions occurs by the transfer of electrons to the electrode by a process similar to that investigated by Gurney, an equation of the type $i = k\mathrm{N}e^{a\mathrm{V}}$, where N is the number of ions in such adsorption positions, would be expected. If N is maintained constant by ion migration during the process the potential should remain constant. The linear fall of the potential during the formation of the adsorbed layer would be explained if the adsorbed oxygen atoms, on account of their electron affinity, behave as dipoles. There would then be a potential difference proportional to the number of adsorbed atoms superimposed on the normal potential difference between the electrode and the charged ionic layer in the solution.

In order to find at what stage of the cathodic polarization this adsorbed layer is destroyed the electrode was polarized cathodically successively to more negative potentials and after each such treatment an anodic curve was taken with a small current. The curves obtained are shown in fig. 2 (*b*) and in Table III the slopes of the linear parts are given.

Table III.

Initial voltage	+1·26	+1·06	+0·96	+0·86
Slope of anodic curve	0·10	0·10	0·15	0·19 × 10^{-3} coulombs/volt.
Initial voltage	+0·76	+0·71	+0·56	+0·36
Slope of anodic curve	0·38	0·86	1·41	1·63 × 10^{-3} coulombs/volt.

So long as the potential does not become more negative than +1·0 volts the slope of the anodic curve corresponds with the capacity of the double layer (1·0 × 10^{-4} coulombs per volt), but at more negative potentials and as the electrode passes along the oxygen depolarization stage the adsorbed layer is gradually reduced as is shown by the increasing quantity of electricity which is required to replace it. The reduction of the adsorbed layer and depolarization by oxygen thus occur simultaneously. In the cathodic depolarization by methylene blue and quinone it was found that the variation of the electrode potential during the process was given by $V = V_0 - RT/{}_{s}F \log q$, where $q = q_0 - it + \alpha + \beta t$ represents the amount of the depolarizer near the electrode after the time t. For oxygen the potential rises more rapidly than according to this equation. This can be explained if it be supposed that the depolarization occurs on those parts of the surface which are covered by oxygen. As this adsorbed oxygen is destroyed the available surface diminishes and the depolarization potential will rise more rapidly than if it were dependent only on the concentration of the depolarizer.

Gold Electrodes in Oxygen Saturated Solutions.

Behaviour in M/10 Sulphuric Acid.—The gold electrodes were made of thin gold foil having an apparent area of 1 cm.^{2}, fused to a thin gold wire which was melted into glass tubes. Typical curves showing their behaviour in dilute (M/10) sulphuric acid are given in fig. 3. The first time-potential curve, of which curve I is an example, was somewhat variable, but afterwards they gave very reproducible curves. As with platinum, in the first anodic treatment a considerable amount of depolarization occurs before the potential reaches a constant value, but if the oxygen overvoltage is allowed to decay for a time and the electrode again made the anode, curve II, the potential falls much more quickly and initially linearly with the time, about $1 \cdot 8 \times 10^{-5}$ coulombs being required in this case for the change of 0·1 volt. As with platinum, this is interpreted as being due to the charging of the double layer without depolarization. When the current is reversed the potential begins to rise linearly at the same rate as in curve III and at $\varepsilon_H = +1 \cdot 1$ a depolarization process begins. When this has proceeded for a time an anodic curve of the first type, curve IV, is obtained on subsequent anodic polarization.

After anodic polarization two definite depolarization stages, α, β, curve V are observed on continued cathodic treatment. The upper stage β, which is in the same region as the single stage observed with platinum is like the latter much reduced by even gentle stirring,* as in curve VI. When similar experiments were made in an atmosphere of nitrogen, the anodic polarization being stopped at +1·8 to avoid the liberation of oxygen, the stage β did not appear although α was well developed. The former is therefore due to cathodic depolarization by molecular oxygen in the solution. Some cathodic depolarization curves in an oxygen saturated solution at a gold electrode which has not been anodically polarized are given in the inset diagram, fig. 3.

The lower stage α, which is quite unaffected by stirring the solution, and remains unaltered even when the electrode has been removed from the solution and washed, must be due to a depolarizer which adheres to the electrode. After long continued anodic polarization the electrode becomes covered with a black film, which is probably an oxide of gold and since this disappears again at this stage during cathodic polarization the process here must be the reduction of this substance. This black substance has been the subject of a number of investigations.† Jirsa and Buryànek found‡ that after drying over sulphuric acid its composition was close to $Au(OH)_3$, and after drying at 142° and over phosphorus pentoxide, the proportion of gold was somewhat less than that required for Au_2O_3.

Curve VII, fig. 3, was obtained on anodic polarization after the potential had been taken cathodically to +0·2. The potential falls linearly from +0·8 to +1·3 (A, A) and then falls slowly along the curve CC, which is similar to

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* This applies to large currents. With small currents the length of the process is increased by stirring, because the rate at which oxygen diffuses to the surface is then an appreciable factor.

† Jirsa and Buryànek, 'Chem. Listy,' vol. 16, pp. 189, 299, 328 (1922); Jirsa and Jelinek, 'Z. Electrochem.,' vol. 30, p. 286 (1924).

‡ 'Z. Electrochem.,' vol. 29, p. 126 (1923).

I but more extended. The quantity of electricity required in the linear change AA is from two to three times that required for changing the potential of the double layer (curve II) at more positive potentials. This is considerably less than would be required to form an adsorbed oxygen layer, as with platinum. It seems likely that the change is merely a double layer effect, but the capacity of the double layer is considerably greater than that at the oxide covered surface.

When the electrode has been taken along the stage β during the cathodic polarization a small break BB appears in the anodic curve at about +1·1, curve VIII, and its length increases as the amount of cathodic polarization in the stage β is increased. It appears to be due to small quantities of a reduction product, formed at the electrode during the cathodic polarization.

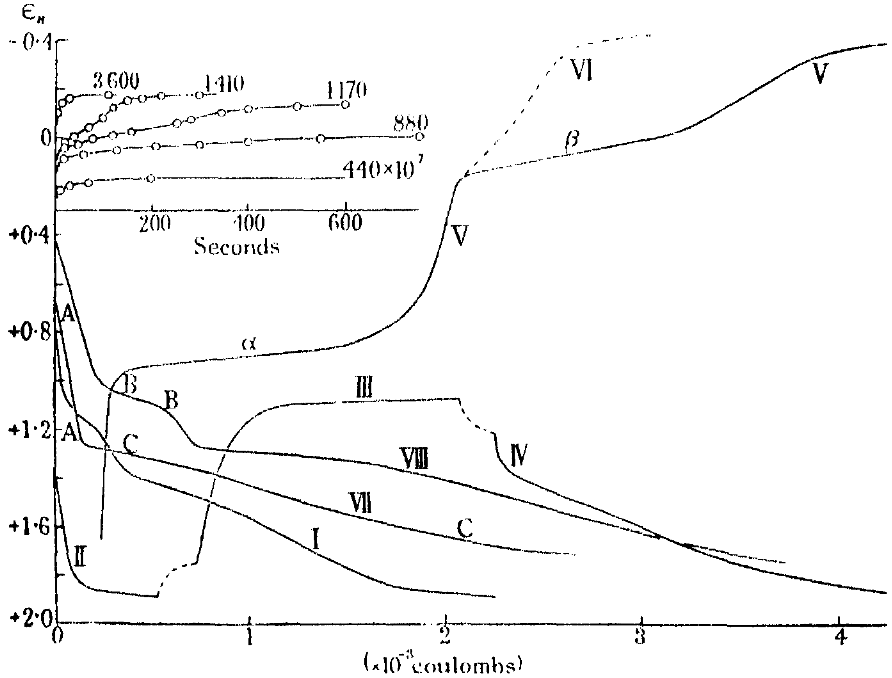

FIG. 3.—Electrochemical behaviour of gold electrodes in dilute sulphuric acid. Curves I–VI, $4\cdot8\times10^{-3}$ amps.; curves VII, VIII, $0\cdot012\times10^{-3}$ amps. Inset diagram: Cathodic curves in oxygen saturated solution, without previous anodic polarization.

The Anodic Process.—The process occurring along CC, fig. 3, had been studied in great detail. The curves obtained with comparatively small currents, with an electrode having a double layer capacity after anodic polarization of about 1×10^{-5} Coulombs/0·1 volt, are shown in fig. 4 (*a*). In order to obtain reproducible conditions the electrode was polarized cathodically to +0·66 before each experiment, after which the solution was stirred with a stream of oxygen for 100 seconds. The total quantity of electricity required to bring the potential to +1·7 volts is nearly constant and is considerably greater than the corresponding amount for platinum electrodes of the same

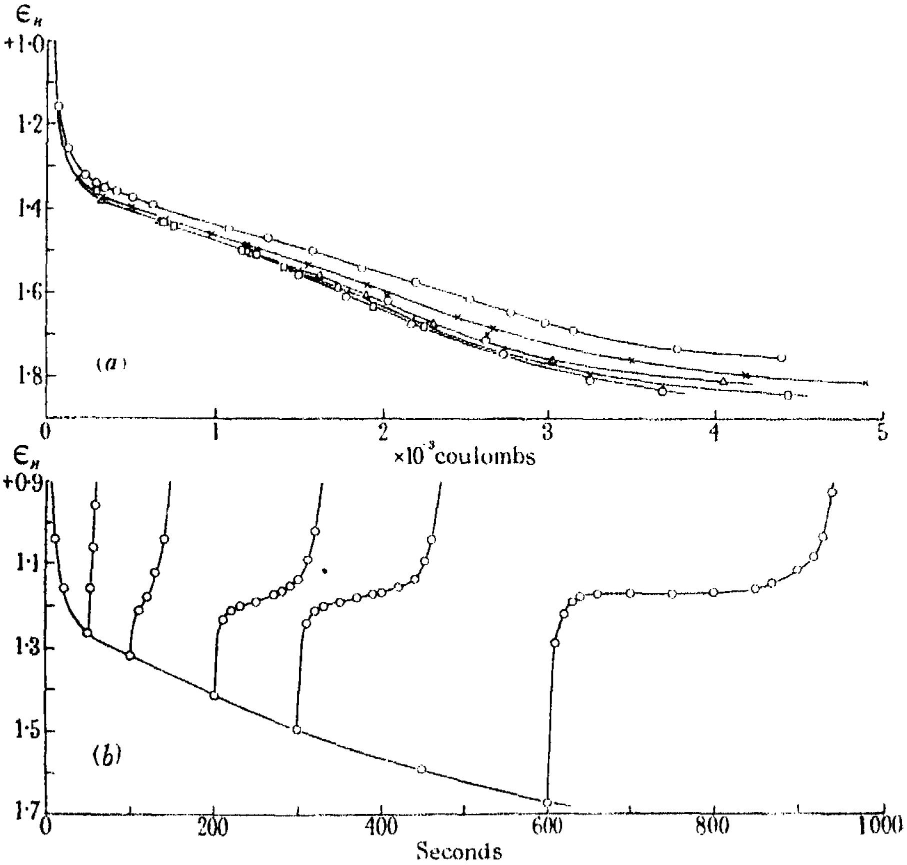

Fig. 4.—(*a*) Anodic polarization of gold electrodes in dilute sulphuric acid.

—○— 63, —×— 137, —△—268,

—□— 442, —○— 684, —○— 2920 × 10^{-7} amps.

(*b*) Cathodic curves after anodic polarization to various stages, 45 × 10^{-7} amps.

capacity. That the formation of oxide occurs along these curves is shown by fig. 4 (*b*), in which the electrode was taken by anodic polarization successively to more positive potentials and the current then reversed. The break α appears in the cathodic curve when the electrode has passed +1·27 and its length increases as the potential falls to lower values down the curve CC. The efficiency of oxide formation, as given by the ratio of the length of the cathodic break α to the amount of anodic polarization initially approaches 100%, but decreases as the process continues, as can be seen from the following table.

Table IV.—Anodic and Cathodic Polarization of Gold Electrodes in M/10 Sulphuric Acid.
Current = 45×10^{-7} amps.

Time of anodic polarization.	Time of anodic polarization below +1·27.	Length of cathodic break.	Efficiency of oxide formation (%).
sec.	sec.	sec.	
50	0	—	—
100	50	50	100
200	150	125	84
300	250	170	68
600	550	340	62
1800	1750	480	27

Jirsa and Buryànek (*loc. cit.*) found by an analytical method that the current yield of oxide when gold electrodes were anodically polarized in 1·1 N . H_2SO_4 at 18° C. was 1·3%. The amount of oxide formed after various periods of anodic polarization can be accurately and simply determined by finding the quantity of electricity required to reduce the oxide by cathodic treatment along the stage α.* The following table shows that this quantity is practically independent of the cathodic current employed.

Table V.—Anodic Polarization, $1 \cdot 9 \times 10^{-3}$ Coulombs with 670×10^{-7} amps.

Cathodic current	670	106	63	13×10^{-7} amps.
Cathodic polarization (to +0·67 volts)	1·54	1·57	1·56	$1 \cdot 42 \times 10^{-3}$ Coulombs

Fig. 5 shows the number of Coulombs passed in the stage α, plotted against the total amount of previous anodic polarization. The inset diagram, curve I, gives a small part of the curve for small anodic polarizations on a much greater scale. The efficiency is high during the early stages of the electrolysis, but it rapidly diminishes, and when the current is continued for a long period the amount of oxide increases linearly with the quantity of anodic polarization the efficiency being about 0·9% (15°). The points shown in the diagram were obtained with currents of $4 \cdot 5 \times 10^{-3}$ amps. and $0 \cdot 069 \times 10^{-3}$ amps. They lie on the same curve and it appears that between these limits at least, the amount of oxide depends on the total amount of anodic polarization and is practically independent of the current density. Some similar measurements at 50° showed that this increase of temperature had little effect on the efficiency.

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* A few measurements of this kind have been made by Shutt and Walton ('Trans. Faraday Soc.,' vol. 28, p. 740 (1932)).

It has been shown that the formation of oxide can be traced without any discontinuity from the appearance of visible amounts to the first stages of the depolarization process at +1·27 volts. The primary process might be either (*a*) the passage into solution of gold ions which are immediately hydrolysed and precipitated as auric oxide or hydroxide, the solubility of which has been shown to be very small in dilute sulphuric acid (Jirsa and Jelinek, *loc. cit.*); or (*b*) the deposition of oxygen atoms in adsorption places at the surface of the electrode, followed by their re-arrangement leading to the formation of definite molecules of gold oxide Au_2O_3, or a hydrated form. The forces between the gold atoms at the surface and those in the underlying layers might be so

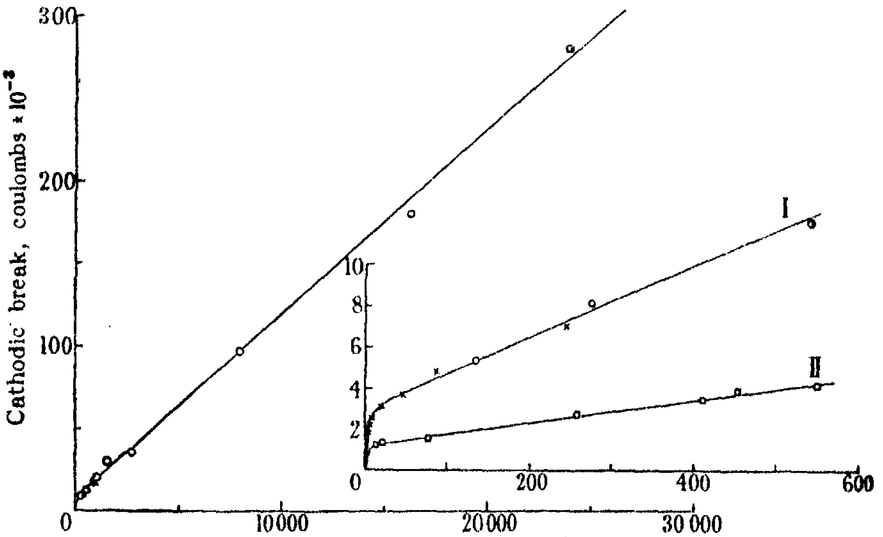

FIG. 5.—*Efficiency of oxide formation at gold electrodes. Anodic currents,*

—○— $4 \cdot 5 \times 10^{-3}$ amps., —×— $0 \cdot 069 \times 10^{-3}$ amps.,
—□— $0 \cdot 37 \times 10^{-3}$ amps.

reduced by the presence of adsorbed oxygen that a re-arrangement, as in the following scheme, could easily occur :—

Au Au . . O	Au (Au_2O_3) Au
Au Au . . O	
Au Au . . O	Au Au
Au Au . . O	Au Au . . O

In order to distinguish between these possibilities it would be necessary to know whether gold ions are capable of dissolving ionically at the potential at which the process begins. Gold dissolves anodically in dilute hydrochloric acid at about the same potential, but this process is probably affected by complex ion formation, in the absence of which a more positive potential would be required. The mechanism (*b*) is thus more probable. In either case as the electrode becomes covered with oxide the effective area of the electrode is reduced and the potential at constant current must fall. It ultimately reaches a value at which the liberation of free oxygen can occur. The oxide is evidently in a porous condition, for it continues to be formed at a slow constant rate even after long electrolysis.

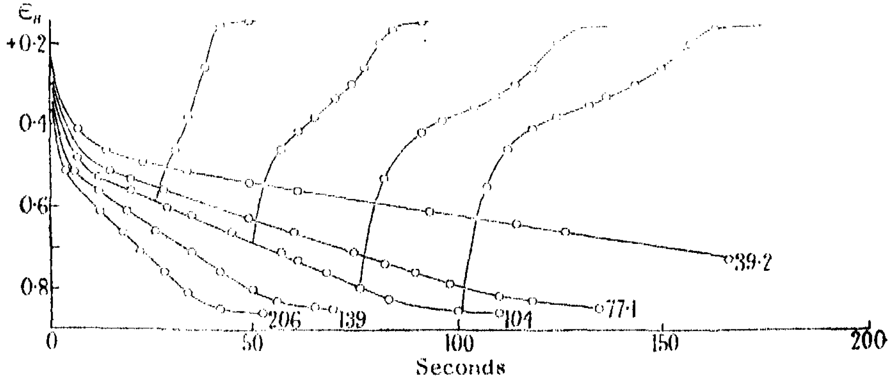

FIG. 6.—Anodic and cathodic curves of gold electrodes in N/10 NaOH. Currents, amps. × 10^{-7}. Cathodic curves with 104 × 10^{-7} amps.

Behaviour in N/10 *Sodium Hydroxide.*—The anodic polarization of gold electrodes in N/10 sodium hydroxide is shown in fig. 6. The curves are linear for a considerable part of their course and are similar to those of platinum in sulphuric acid. The following table gives the quantity of electricity required for a change of 0·1 volt in the linear region.

Table VI.—Double Layer Capacity of Electrode, $1 \cdot 3 \times 10^{-5}$ Coulombs/$0 \cdot 1$ volt.

Current	24·3	39·2	77·1	104	139	206×10^{-7} amp.
Coulombs for 0·1 volt	2·55	2·51	2·39	2·39	2·23	$2 \cdot 16 \times 10^{-4}$

The ratio of these quantities to the double layer capacity of the electrode is not much greater than that observed for platinum. After anodic polarization a distinct depolarization stage appears in the cathodic curves, of which examples are shown in fig. 6, at about +0·3. This stage is not so flat as in the corresponding curves in the acid solution, but the process is quite distinct from the oxygen depolarization which begins at +0·16. The quantity of electrolysis required for this process after varying periods of anodic polarization is given in Table VII.

Table VII.—Anodic and Cathodic Current, 104×10^{-7} amps.

Time of anodic polarization	26	50	75	100 seconds
	200	300	600	1560 seconds
Anodic polarization	0·27	0·52	0·78	$1 \cdot 05 \times 10^{-3}$ Coulombs
	2·08	3·12	6·24	$16 \cdot 2 \times 10^{-3}$ Coulombs
Cathodic polarization to +0·2	0·15	0·43	0·51	$0 \cdot 58 \times 10^{-3}$ Coulombs
	0·64	0·72	0·79	$0 \cdot 83 \times 10^{-3}$ Coulombs

With this current the potential fell linearly on anodic polarization for 90 seconds. As the electrode passes down this linear stage the subsequent cathodic process increases steadily in length, but when the linear fall of potential is completed the rate of increase becomes very small. The following figures obtained with another electrode of rather greater capacity show that the length of this stage continues to increase at a very slow rate even after long continued anodic polarization.

Table VIII.

Anodic polarization	24	307	768	4620	27200×10^{-3} Coulombs
Cathodic break	1·19	1·36	1·43	1·64	$1 \cdot 72 \times 10^{-3}$ Coulombs

It is evident that the greatest amount of electrolysis required here in the cathodic process is of the same order as that required to remove a single layer of oxygen atoms at the surface of the electrode. The fact that the anodic process begins at a more negative potential than is required for the ionic solution of gold, and the similarity between the anodic curves and those of platinum, suggest that the primary process is the same as that postulated for the latter, viz., the formation of an adsorbed layer of oxygen atoms.

At an electrode which had previously been used for the determination of the efficiencies of oxidation in sulphuric acid, however, a considerable amount of oxidation occurred, although the amount, fig. 5, curve II, was less than under similar conditions in sulphuric acid. For example, after 10 Coulombs had been passed with a current of $5 \cdot 6 \times 10^{-3}$ amps., 66×10^{-3} Coulombs were required to reduce the oxide formed as compared with 120×10^{-3} Coulombs in sulphuric acid. It therefore appears that the electrode which has previously been oxidized and reduced in sulphuric acid is much more open to attack in alkaline solution than one which has not been so treated.

Action of Reducing Agents on the Oxide Films.—When platinum electrodes have been anodically polarized in solutions containing hydrogen, the potential returns in a short time at open circuit to the neighbourhood of the reversible hydrogen potential. After anodic polarization under similar conditions the potential of gold electrodes did not become more negative than $+1 \cdot 2$ even after a considerable time. If any reduction of the oxide by hydrogen occurs it is a very slow process. However, reducing agents such as potassium ferrocyanide and hydroquinone are able to reduce the oxide. After anodic polarization in solutions containing these substances the potential becomes rapidly more negative to the point at which the reduction of oxide occurs, remains nearly constant for a time during its reduction and then changes further to the reversible potential characteristic of the solution. On account of the close resemblance between this process and the spontaneous recovery of the potential of anodically passivated gold in solutions of chlorides (Shutt and Walton, *loc. cit.*) some observations were made of the variation of the time of recovery with the concentration of the reducing agent, which are given in Table IX.

Table IX.—Reduction of Gold Oxide by Hydroquinone.

N/10 Sulphuric acid. Anodic polarization, $1 \cdot 0 \times 10^{-3}$ amps. for 30 seconds.

Concentration of hydroquinone, gm./litre	0·33	0·67	1·00	2·00	3·00	—
Time of recovery (seconds)	59	27	17	6·5	1	—

N/10 Sodium hydroxide. Anodic polarization, $0 \cdot 5 \times 10^{-3}$ amps. for 5 seconds.

Concentration of hydroquinone, gm./litre	0·01	0·015	0·02	0·03	0·05	0·10
Time of recovery (seconds)	98	59	38	22	9·5	3·5

The concentration of hydroquinone for a given time of recovery is much less in alkaline than in acid solution. Except for the shortest times the results are in accordance with the equation $tc = \mathrm{K} - ac$, where t is the time of recovery and c the concentration of hydroquinone and K and a are constants having the values 21 and 4 in M/10 H_2SO_4, and 1·1 and 14 in N/10 NaOH. The comparatively small term ac apparently represents the amount of reduction of the oxide layer by hydroquinone during the anodic process. The rate of reduction, as represented by the reciprocal of the time, is therefore proportional to the concentration of hydroquinone. It is significant that Shutt and Walton (*loc. cit.*) found a similar relation between the time of the spontaneous recovery of passivated gold in solutions of chlorides and the hydrogen ion concentration. The nature of the reduction process in this system has not, however, been definitely established.

We wish to express our gratitude to the Carnegie Trustees for a Scholarship held by G. A., and a Teaching Fellowship held by J. A. V. B., and to the Committee of the Moray Fund and Imperial Chemical Industries, for grants for photographic paper and apparatus.

Summary.

(1) Experiments are described which support the view that on the anodic polarization of platinum electrodes in sulphuric acid or alkaline solutions a single layer of adsorbed oxygen atoms is formed. On cathodic polarization, the reduction of the adsorbed layer occurs simultaneously with depolarization by dissolved oxygen in the solution.

(2) When gold electrodes are polarized in dilute sulphuric acid, the formation of a definite oxide begins when the potential reaches +1·27 volts. The efficiency of oxide formation, which is about 100% in the earliest stages, steadily decreases as the electrolysis proceeds and finally reaches a constant value of about 0·9%. In alkaline solutions the behaviour of gold is very similar to that of platinum, and even after long continued electrolysis the amount of oxidation is not more than corresponds with a single layer of oxygen atoms at the surface. The reduction of the oxide or oxygen films by hydroquinone has been studied.

The Structure of Surface Films. Part XX.—Surface Potential Measurements on Nitriles.

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(From the Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London, and Imperial Chemical Industries, Ltd.)

(Communicated by F. G. Donnan, F.R.S.—Received June 16, 1933.)

This paper extends the measurements on the change in contact potential caused by a monomolecular insoluble film, at an air-water interface, to the series of nitriles, $C_nH_{2n+1}CN$. The length of the carbon chain was varied from 14 to 22 total carbon atoms, including the carbon in the end CN group. The nitriles were chosen because their end group, CN, is one of the few organic groups in which the resultant dipole moment of the end group cannot be altered by internal rotation of the various parts of the group. In nearly all previous studies, those on the fatty acids,[*][†] alcohols, esters,[‡] a comparison of the vertical component of the dipole moment of the molecules in the films, with the moments of similar molecules in free space, is hindered by the very large variations which might occur in the resultant dipole moment of a polar group, when the atoms of the group assume different relative positions owing to rotation round the linkages between atoms. For instance, using Eucken and Meyer's data for the component parts of the dipole of the carboxyl group, the vertical component of the total dipole moment can assume any value between $-4\cdot2$ and $+13\cdot2 \times 10^{-19}$ e.s.u.[§]

The experimental technique was the same as that described in our previous paper (*loc. cit.*), except that sometimes a copper wire bearing a little polonium at the lower end was used in place of the disc. This renders it somewhat easier to detect inhomogeneities in the film. Simultaneous measurements were taken of surface pressure and surface potential. All experiments were done at room temperature, which was never above 23·5° C. or below 16° C. Petroleum ether (60–70° C.) was used as the solvent for dropping on the surface in all experiments; the underlying solution was N/100 hydrochloric acid.

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[*] Schulman and Rideal, 'Proc. Roy. Soc.,' A, vol. 130, p. 259 (1931).

[†] Adam and Harding, *ibid.*, vol. 138, p. 411 (1932).

[‡] Schulman and Hughes, *ibid.*, vol. 138, p. 430 (1932).

[§] Adam and Harding, *loc. cit.*, pp. 427–8.

Results.

Fig. 1 gives the results on the 18, 20, and 22 carbon nitriles, the last two of which form condensed films only at the temperature of experiment. Fig. 2, on the 17 carbon nitrile, which forms a liquid expanded film and also shows the transition to the condensed state. Fig. 3 exhibits the values for the 14 and 16 carbon nitriles, which form liquid expanded films only. The curves show the surface pressure, F, the surface potential change, ΔV, due to the film, and μ, calculated from the equation

$$\Delta V = 4\pi n \mu \tag{1}$$

plotted against A, the area per molecule, and n, the number of molecules per square centimetre in the film. μ is related to the vertical component of the dipole moment of the molecules in the film; its meaning will be discussed later in this paper.

The surface-pressure area curves agree well with previously published results. The condensed films tend, at zero compression, to an area of 27 sq. A., and their films are moderately compressible, indicating some re-arrangement, or possibly some compression of the polar end groups, on compressing the film. The large size of the end groups is no doubt due to the great amount of space required by the three valencies between carbon and nitrogen

$$—C\equiv N$$

which start out from the terminal carbon atom at angles of about 109½° to the bond joining the end carbon to the next one in the chain. The carbon and nitrogen, if singly bound, would not occupy more than the usual area (20·4 sq. A.) for hydrocarbon chains closely packed, so that the area of 27 sq. A. must be ascribed to the bulge formed by the three linkages at the end of the molecule.

The surface potential, in the wholly condensed films of the 20 and 22 carbon nitriles, was constant within 10 millivolts, below 27 sq. A., at which area the film first becomes closely packed. From 27 to 25 sq. A. the value of μ was constant, falling slightly on compression to smaller areas. At larger areas than 27 sq. A. the surface was very heterogeneous, the fluctuations amounting to hundreds of millivolts; this indicates without doubt that there are two surface phases present, namely, coherent islands of condensed film, in equilibrium with vapour film.

Stearic nitrile appears, from the surface pressure curve alone, to be nearly completely condensed; below 8 dynes per centimetre, however, the areas are slightly larger for a given pressure than for the longer chain nitriles. Between 26 and 30 sq. A. there are fluctuations of the order 50 mv., *i.e.*, similar to those observed in the transition region between condensed and *liquid expanded* films with the 17 carbon nitrile. It appears, therefore that this film is not completely condensed below 8 dynes per centimetre. Even at higher pressures the potential is some 50 mv. less than for the two higher homologues; it appears doubtful therefore if stearic nitrile is completely condensed at any pressure.

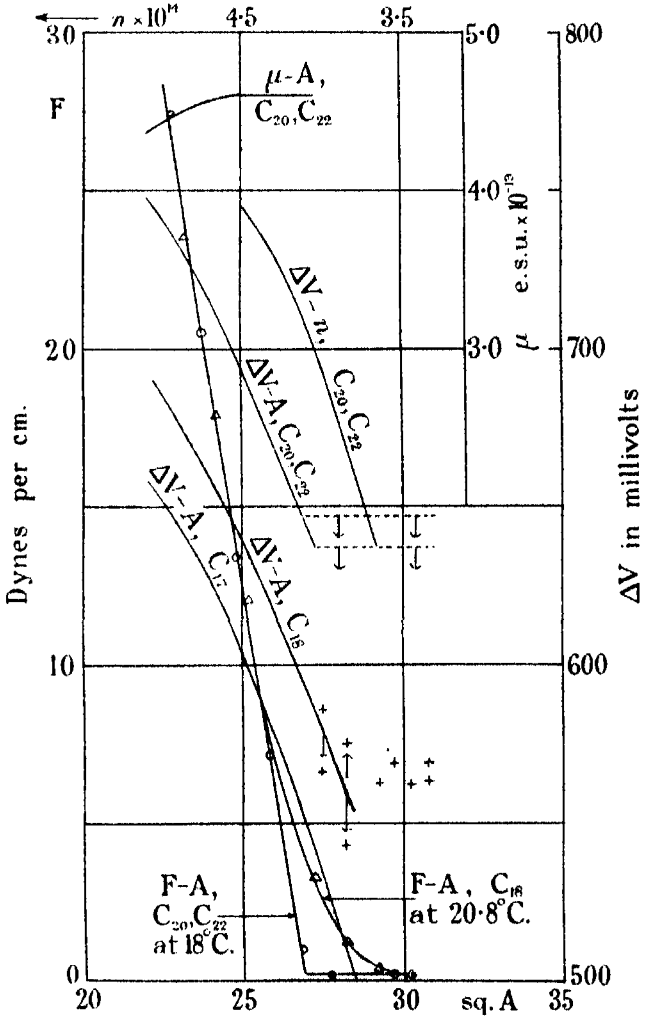

Fig. 1.—Condensed nitrile films.

The 17 carbon nitrile, margaric, forms an expanded film at 18·9° C. at pressures below 5 dynes per centimetre ; at this pressure and 34 sq. A. there is the usual sudden change in direction of the surface pressure curve, characteristic of the commencement of the transition from expanded to condensed film. The potential curve also shows a fairly abrupt change in direction at this area ; and also, at the same area, marked fluctuations in potential appear, amounting

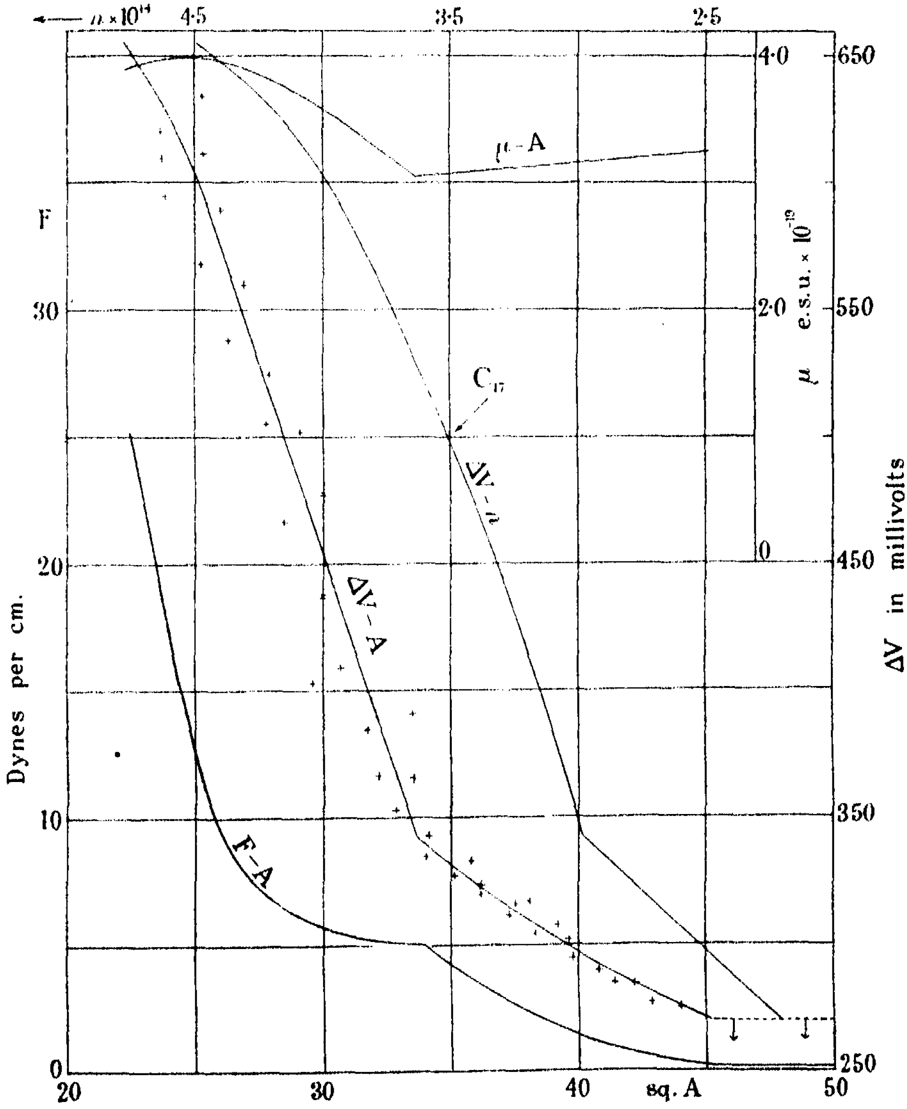

FIG. 2.—Margaric nitrile.

to 50 or 70 mv. At areas between 34 and 46 sq. A. the fluctuations are certainly not more than 10 mv. This is a perfectly clear example of inhomogeneity of the surface in the transition region between expanded and condensed film; the inhomogeneities persist down to 24 or 25 sq. A., so that it seems that the film is not completely condensed even at this area and a pressure of 35 dynes per centimetre. The limiting area, at low compressions, of the expanded film is about 46 sq. A.; above this area very large fluctuations of potential commence, indicating that there are both liquid expanded and gaseous films present.

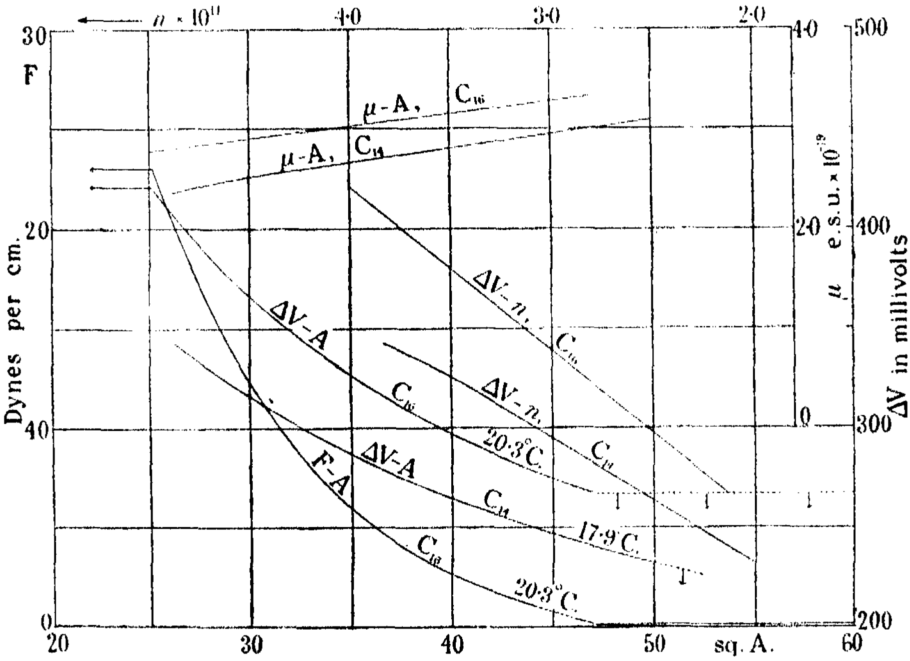

Fig. 3.—Expanded nitrile films.

μ decreases slightly with decreasing area in the expanded film, in the transitional region there is a decided rise in the *average* value of μ as the area is diminished.

The 14 and 16 carbon nitriles, fig. 3, give liquid expanded films; the 16 carbon having a limiting area of 47 sq. A., and the 14 carbon of about 50 sq. A. The potentials were uniform within 10 mv. below this limiting area; above this area large fluctuations were found, the value of 267 mv. persisting in patches some distance beyond 47 sq. A. with palmitic nitrile; while with myristic nitrile, though it was more difficult to obtain coherent islands of 230 mv. of any considerable extent, the potential fluctuated between about this value and practically nothing. There is less lateral adhesion between the molecules in films of myristic nitrile than with palmitic nitrile. The surface pressure curves of Adam and Jessop* are not conclusive as to whether myristic nitrile is a liquid expanded (coherent) film or a vapour expanded film; it is now clear, from the magnitude of the fluctuations observed just above 50 sq. A., that the film of myristic nitrile is just below the critical point at which the liquid expanded film ceases to exist, not just above that point, as was surmised from the earlier measurements of surface pressure. A re-determination of the surface pressure curve at large areas now indicates that there is a region of constant surface vapour pressure, extending from 50 to 450 ± 50 sq. A., having a pressure of 0·39 ± 0·02 dynes per centimetre.

μ decreases slightly with decreasing area, just as with the expanded part of the film of margaric nitrile.

Discussion of Results.

(1) There is a marked discontinuity in the surface potential curve with margaric nitrile, where the expanded film ceases and the transition region to condensed film commences; at the same time the value of μ begins to rise sharply, and the film is markedly inhomogeneous in the transition region. In the previous work with myristic acid we failed to notice any sharp change at this point, or fluctuations in the transition region except when there was a probability of collapse of the film having occurred. On the other hand, Schulman and Rideal, and later Schulman and Hughes, found small fluctuations in the transition region with myristic acid and believed this transition to be heterogeneous. Since, with myristic acid, the value of μ does not change appreciably on passing from the expanded to the condensed film, the smallness of the fluctuations in the transition region does not necessarily mean that the film is homogeneous. With margaric nitrile the film is clearly inhomogeneous in the transition region.

The surface pressure is never constant during a transition from expanded to condensed films; a great many such transitions have now been investigated. In the only other type of transition in the films, where definite evidence of two types of co-existent film has been found, namely, the transition from coherent to vapour films, the surface pressure is constant. Reasoning by analogy with heterogeneous equilibria in three dimensions, and regarding the material of the spread film as the only component present, one might expect a two-dimensional analogue of the phase rule to hold; *i.e.*, there should be a *constant* surface pressure wherever there are two co-existent types of film. Such an analogy has the weakness, however, that the relative numbers of molecules of water and of the spread material in the film are varying during compression; it appears incorrect to apply a two-dimensional analogue of the phase rule in its simplest form, considering the spread material as the only component, and the surface pressure as the analogue of vapour pressure.

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* 'Proc. Roy. Soc.,' A, vol. 110, p. 428 (1926).

(2) *Interpretation of* μ.—μ, calculated from equation (1), is often referred to as the " vertical component " of the dipole moment of the film per molecule. If the film could legitimately be considered as a parallel plate condenser, having the upper ends of the molecular dipoles as the upper, positively charged sheet, and the lower ends as the lower (negative) sheet, and if the dielectric constant of the space between these sheets could be taken as unity, then μ would be the vertical component of the dipole moment of the molecules in the film. An average value of the total dipole moment of the nitrile group is about 35×10^{-19} e.s.u.*; μ varies between $2 \cdot 4$ and $4 \cdot 6 \times 10^{-19}$. Thus the maximum value of μ is only about one-seventh of the total dipole moment of the nitrile group; it is always found that μ is much less than the dipole moment of the polar groups in a film on water. For the nitriles, μ increases considerably from the expanded to the condensed states, and it seems probable that this increase is due to the dipoles of the nitrile groups becoming oriented more nearly perpendicular to the surface. Below about 27 sq. A., however, when the films are condensed, μ is nearly constant; the slight fall at areas less than 25 being possibly not real, but due to errors in the calculation caused by neglecting collapse of the films under high pressure. If we assume that the dipoles are perpendicular to the surface in the condensed films,† where μ is nearly constant and a maximum, the dielectric constant in the films is seen to be about 7. This is of the order one-eleventh of the dielectric constant of water, a reasonable value, perhaps, when it is considered that the " dielectric constant " of the principal space intervening between the ends of the dipoles, namely, the substance of the molecules forming the film, could not appear in this calculation; and the greater part of the dielectric constant of the film must be due to a re-orientation of water molecules lying close to and between film molecules, under the influence of the oriented dipoles of the film molecules.

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* Smyth, " Dielectric Constant and Molecular Structure," Appendix I.

† This assumption cannot be substantiated at present, but if the dipoles are not quite vertical, there will still probably be quite a large dielectric constant in the films.

The difficulties in a quantitative interpretation of the surface potential in terms of the dipoles of the film molecules and their orientation have been well indicated by Frumkin and Williams*; we feel that there is some justification for supposing that, as μ increases, the axis of the dipoles usually becomes more nearly perpendicular to the surface, but a thorough quantitative treatment of the subject seems lacking at present.

One of us (J. B. H.) thanks the Department of Scientific and Industrial Research for a grant.

Summary.

Surface potential measurements on monomolecular films of long chain nitriles indicate a maximum value of μ, calculated from the simple Helmholtz equation, only about one-seventh of the dipole moment of the nitrile group as obtained by other methods. In the nitrile group there is no possibility of modification of the value of the dipole by internal rotation of the different parts of the polar groups, hence the effective "dielectric constant" of the surroundings of the film molecules is probably of the order 7.

The transition between condensed and expanded films is unquestionably heterogeneous with the nitriles.

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* 'Proc. Nat. Acad. Sci., Wash.,' vol. 15, p. 400 (1929).

λ 3240 *Band of* NH.

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(Communicated by A. Fowler, F.R.S.—Received June 17, 1933.)

[Plate 2.]

Introductory.

Recently, during use of a heavy current discharge tube for producing the continuous spectrum of hydrogen, it was observed that the well-known λ 3360 band of NH was very well developed when there was a trace of nitrogen in the tube. It was further observed that the band thus produced did not exhibit the strikingly symmetrical structure shown in the ammonia-oxygen flame. This loss of symmetry was found to be due to the presence of a second band at λ 3240, degraded to the red and overlapping the R-branch of the λ 3360 band. The new band also showed the open structure characteristic of light hydride molecules; the spacing of its lines indicating a molecular weight about that of NH.

Considering the proximity of this band to the λ 3360 band it seemed strange that it should not be equally well known. An examination of the NH spectrum as obtained under various other conditions was therefore made. A. Fowler and Gregory* have published photographs obtained from the oxy-ammonia flame and from imperfectly dried cyanogen burning in an atmosphere of oxygen. The λ 3240 band is absent in both cases, although the λ 3360 band appears with great intensity. On the other hand, it appears strongly together with the λ 3360 band in the chemi-luminescence spectrum of N_3Cl and HN_3 obtained by K. Gleu.† It was also obtained in spectra due to excitation of ethyl and propyl iodides by active nitrogen in certain experiments made by Dr. H. T. Byck.‡

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* 'Phil. Trans.,' A, vol. 218, p. 351 (1919).

† 'Z. Physik,' vol. 38, p. 176 (1926). Gleu's photograph, which shows an exceedingly heavy exposure on a small dispersion spectrograph, also exhibits other bands grouped symmetrically about the λ 3360 band. These are evidently higher vibrational members of the same system. For, since $B'_0 \; i \div B''_0$ for the (0, 0) band at λ 3360 and since B'_0 is always greater than B'_1 and B''_0 is always greater than B''_1 we should expect bands to the violet of λ 3360 to degrade to the red and those to the red of λ 3360 to degrade to the violet if they belong to this system. This is just what is observed in Gleu's photograph.

‡ Private communication.

It is to be noticed that the spectra from which the band is absent are those produced in flames, whereas those in which it is present are produced by processes where greater energy is available for excitation. From this observation it would appear that considerably greater energy is required to excite the λ 3240 band than to excite the λ 3360 band. Since the bands are in the same region of the spectrum this would further indicate that both levels involved in the emission of the λ 3240 band are distinct from those involved in the emission of the λ 3360 and that the lower level of the λ 3240 band is excited to a considerable extent.

Experimental Procedure.

The discharge tube was of the water-cooled, heavy-current type described by Lawrence and Edlefsen* for use as an intense source of continuous ultra-violet light. It was excited by the uncondensed discharge from a transformer taking a current of 2·5 amps. at about 3000 volts.

In order to obtain NH bands as free as possible from overlapping bands of the second positive system of N_2, which is also produced by this source, the proportion of nitrogen in the tube was made very small. This, of course, led to decreased intensity of emission of both the NH and N_2 systems, but the falling off was much more rapid in the case of the N_2 bands as was expected. The amount of nitrogen was decreased step by step until the intensity of the second positive bands became negligible in comparison with that of the NH bands. On the plates thus taken, the variations in intensity of the λ 3240 band were always consistent with those of the λ 3360 band and were quite independent of the presence of small quantities of carbon or oxygen in the tube.

Good photographs were obtained in the first and second orders of a 21-foot concave grating employing the Paschen type of mounting. The second order was used for measurements, giving a dispersion of 1·3 A./mm. and resolving lines separated by more than 0·03 A.

Structure of the Band.

Under flame conditions the λ 3360 band shows two very strong central maxima of intensity at λλ 3360, 3370. These are formed by the Q-branches of the (0, 0) and (1, 1) bands respectively. On either side of the central maxima is a series of triplets decreasing both in separation and intensity with distance from the centre. The series to the violet is the R-branch ; that to the red the P-branch. They are symmetrically arranged about the Q-branch because

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* 'Rev. Sci. Instr.,' vol. 1, p. 45 (1930).

$B'_0 \div B_0''$. Under discharge-tube conditions the R-branch does not appear to fade out gradually in a manner similar to the P-branch but shows a rise in intensity and comes to a clearly defined head at λ 3240. Under high dispersion this change in appearance is seen to be due to the superposition of a band degraded to the red. This is shown in Plate 2.

This new band is found to consist of a P-branch, a Q-branch and an R-branch, each of which exhibits a very narrow doubling, increasing in magnitude with increasing value of K. The continuity of the P and R branches through the origin is broken by four missing lines, three of which are on the R-branch side of the first member of the Q-branch. The distribution of intensity is such that early members of the P-branch are slightly stronger than those of the Q-branch while the early members of the R-branch are much weaker. These features are those characteristic of a band arising from an electron transition of the type classed as $^1\Pi \rightarrow {}^1\Delta$. The fine structure doubling can be immediately explained on this interpretation as arising from Λ-doubling of the energy levels. Theoretically, Λ-doubling is to be expected in both the $^1\Pi$ and $^1\Delta$ states, but should be of much greater magnitude in the former. The analysis of the band shows that the whole of the observed doubling may be attributed to the $^1\Pi$ state within observational error.

Analysis of the Band.

W. Jevons in his "Report on Band Spectra of Diatomic Molecules" has pointed out that very few bands are known involving transitions between $^1\Pi$ and $^1\Delta$ levels. The only $^1\Delta \rightarrow {}^1\Pi$ bands which have been analysed are those of the orange system of He_2 ((0, 0) and (1, 1) band near λλ 6110 and 6131). The type of structure associated with this transition is illustrated by the yellow band of He_2 near λ 5730, which is really a $^3\Delta \rightarrow {}^3\Pi$ band with the spin tripling unresolved. No bands involving the transition $^1\Pi \rightarrow {}^1\Delta$ appear to have been observed. Since the λ 3240 band of NH illustrates the theoretical structure to be expected for this transition very beautifully it is perhaps desirable to describe it in some detail. The nomenclature used for this purpose is that which has been generally adopted.*

Neglecting at first the rotation of the molecule as a whole, it is found convenient to picture the spins of the various electrons as yielding a resultant spin angular momentum S, while their orbital angular momenta combine together to give a resultant L. Owing to the axial symmetry of the field L precesses rapidly about the internuclear axis giving a quantized component Λ along this axis. If the magnetic field associated with this is sufficiently strong S is also coupled to the axis giving a component Σ. Ω is used to denote the resultant Λ + Σ. The molecular states are described as Σ, Π, Δ, ..., according as Λ = 0, 1, 2, ..., etc., and are singlet, doublet, triplet, ... according as S = 0, $\frac{1}{2}$, 1, ..., etc.

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* For details of this see Mulliken, "Rev. Mod. Phys.," vol. 2, pp. 60 and 506 (1930); vol. 3, p. 89 (1931) and vol. 4, p. 1 (1932); or Jevons, "Report on Band Spectra of Diatomic Molecules" (1932).

Rotation of the molecule as a whole introduces the angular momentum of the nuclei perpendicular to the internuclear axis and this interacts magnetically with the other angular momenta. The energies of the resulting states depend on the relative magnitudes of the various interactions. Hund has distinguished four limiting cases which he calls *a*, *b*, *c* and *d*. Cases *a* and *b* are by far the most common.

In *case a*, S is strongly coupled to Λ to give a component Σ along the internuclear axis, and Ω is quantized. With the nuclear angular momentum Ω gives a total resultant angular momentum of $h/2\pi\sqrt{J(J+1)}$ where the quantum number J takes the values Ω, Ω + 1, Ω + 2, ...

In *case b*, S is not coupled to Λ. The nuclear angular momentum with Λ gives a resultant angular momentum of $h/2\pi\sqrt{K(K+1)}$ where K takes the values Λ, Λ + 1, Λ + 2, ... As K increases S interacts to a small extent with it and the two precess around their resultant, again denoted by J.

In the special case of singlet states where S = 0 both cases yield the same result and J = K. This is commonly called case *b′* and is that holding for the λ 3240 band.

The rotational energy terms in this case are given by

$$F(K) = B_v [K(K+1) - \Lambda^2] + D_v K^2(K+1)^2 + \ldots$$

Substituting Λ = 1 for the upper $^1\Pi$ state, and Λ = 2 for the lower $^1\Delta$ state and adding terms to represent electronic and vibrational energy, we obtain for the total energy term of the initial state of the λ 3240 band

$$T' = T'_e + G'(v) + B'_v [K(K+1) - 1] + D'_v K^2(K+1)^2 + \ldots$$

where K = 1, 2, 3, ..., and for the final state

$$T'' = T''_e + G''(v) + B''_0 [K(K+1) - 4] + D''_0 K^2(K+1)^2 + \ldots$$

where K = 2, 3, 4, ...

The rotational levels given by these expressions are each split into two component levels—the so-called Λ doubling. Kronig* has calculated from perturbation theory the amount of this splitting. Using wave-number units throughout it is :—

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* "Band Spectra and Molecular Structure," p. 50.

for $^1\Pi$ levels

$$\Delta T = \text{const.}\, K(K+1),$$

for $^1\Delta$ levels

$$\Delta T = \text{const.}\, (K-1)\, K(K+1)(K+2).$$

The constant is given as $B_0 (B_0/\nu)^{2\Lambda-1}$ where ν is of the order of magnitude of an electronic frequency. This constant is small and in the case of the $^1\Delta$-state too small to allow the splitting to be observed. The component levels are divided into two classes, *positive* and *negative*, according to the properties of the wave-mechanical functions representing them. Transitions occur only between levels of opposite types. The further selection rule that $\Delta K = \pm 1, 0$ gives rise to the three branches. This is represented in fig. 1.

Table I gives the wave-numbers of the P, Q and R branches of the band corresponding to the various values of K. The two components of the Λ-doublets are written together. Table II gives the rotational term differences for the initial and final levels. These are defined as follows :—

$$\Delta_2(K)' = F'(K+1) - F'(K-1),$$
$$\Delta_2(K)'' = F''(K+1) - F''(K-1)$$

and are obtained by combining the wave-numbers of the lines as follows :—

$$\Delta_2(K)' = R(K) - P(K)$$
$$\Delta_2(K)'' = R(K-1) - P(K+1).$$

The relations may be checked by reference to fig. 1. The term differences are then used to calculate the constants in the expressions for the rotational energy given above. The values of the moment of inertia I and the internuclear distance r are obtained from the relations.

$$B\,.\,I = 27\cdot 66 \times 10^{-40}.$$
$$I = r^2 M_1 M_2/(M_1 + M_2).$$

The difference of energy between the two levels exclusive of rotational energy is given as ν_0. The following values are obtained for these constants :—

$$\nu_0 = 30704\cdot 13 \text{ cm.}^{-1}.$$

$B'_0 = 14\cdot 147 \text{ cm.}^{-1}.$	$B''_0 = 16\cdot 460 \text{ cm.}^{-1}.$
$D'_0 = -2\cdot 20 \times 10^{-3} \text{ cm.}^{-1}.$	$D''_0 = -1\cdot 90 \times 10^{-3} \text{ cm.}^{-1}.$
$I'_0 = 1\cdot 955 \times 10^{-40} \text{ g. cm.}^2.$	$I''_0 = 1\cdot 680 \times 10^{-40} \text{ g. cm.}^2.$
$r'_0 = 1\cdot 123 \times 10^{-8} \text{ cm.}$	$r''_0 = 1\cdot 041 \times 10^{-8} \text{ cm.}$

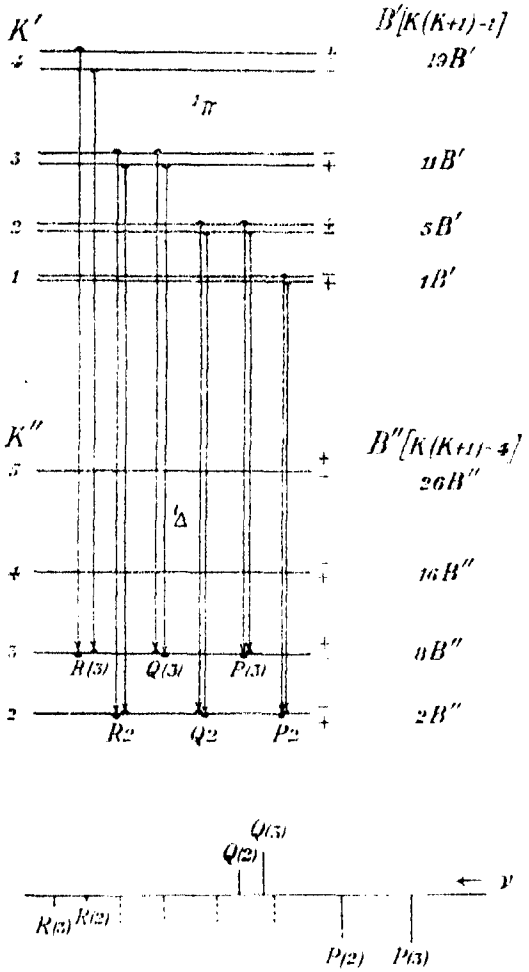

Fig. 1.—Diagram showing the branches resulting from a $^1\Pi \rightarrow {}^1\Delta$ transition. The Λ-doubling of the $^1\Pi$ levels is much exaggerated. The positive and negative signs may be interchanged since the analysis gives no means of deciding between the alternative arrangements. Below are shown the relative positions in the spectrum of the first two members of each branch. The length of line is proportional to the "intensity factor." The dotted lines indicate the positions of the four "missing lines." The Λ-doubling is omitted for simplicity.

Table I.—Branches of NH band λ 3240.

K.	P(K).	Q(K).	R(K).
2	30685·42	30741·94	30826·56
3	43·50	28·11	40·85 40·64
4	30597·05	09·81	50·31 49·80
5	46·16 45·68*	30686·68 86·20	54·74 54·02*
6	30490·83 90·30	58·86 58·19	54·02* 53·08
7	30·88 30·22	26·09 35·20	48·10 46·93
8	30366·37 65·43	30588·39 87·24	36·70 35·27
9	30298·51 97·31	45·68* 44·13	19·83 18·00
10		30497·52 95·73	30797·04 94·89
11		44·03 42·01	68·32 65·76
12		30384·96 82·42	33·23 30·33
13		20·29 17·20	

* Blended lines.

Since the band is the only one of its system which is observed, no direct value of ω_0 can be obtained but approximate values have been estimated by use of the formula*

$$\omega_0{}^2 = -\frac{4B_0{}^3}{D_0},$$

which yields

$$\omega'_0 = 2270 \text{ cm.} \qquad \omega''_0 = 3060 \text{ cm.}$$

Table III gives the separations of the Λ-doubling in the $^1\Pi$ state for various values of K. In the third column these separations are divided by K(K + 1) and the result shown to be constant. The fact that the narrow doublets

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* Strictly this formula is only justified for the values of these constants at the equilibrium internuclear distance r_e, that is in the form $\omega_e{}^2 = -4B_e{}^3/D_e$. In general, however, the relation appears to hold quite well as used above.

R(K − 1), Q(K) and P(K + 1) are equal within observational error, and that the series of $\Delta_2(K)''$ values show no systematic deviation requires that the whole of the observed doubling be attributed to the $^1\Pi$ state. It can be expressed up to the highest value of K observed, namely, K = 13, by the formula

Table II.—Rotational Term Differences.

K.	$\Delta_2(K)'$.	$\Delta_2(K)''$.
2	141·14	
3	197·35 197·14	229·51
4	253·26 252·75	294·69 294·96*
5	308·58 308·34*	359·48 359·50
6	363·19* 362·78	423·86 423·80*
7	417·22 416·71	487·65* 487·65
8	470·33 469·84	549·59 549·62
9	521·32 520·69	

* Term derived from blended lines.

Table III.—Λ-doubling of the $^1\Pi$ state.

K.	$\Delta\nu$.	$\Delta\nu/K(K+1)$.
4	0·28	0·014
5	0·51	0·017
6	0·68	0·016
7	0·92	0·0164
8	1·17	0·0163
9	1·49	0·0165
10	1·81	0·0165
11	2·09	0·0163
12	2·15	0·0163
13	3·00	0·0165

$$\Delta\nu = 0{\cdot}0164\ K(K+1).$$

If this constant is equated to B^2/ν taking B = 14 it yields an electronic frequency about 12,000 cm.$^{-1}$.

Intensity Distribution.

The intensity of emission of a line of the band is usually given by a formula of the type*

$$\text{Int.} = Ci\,\varepsilon^{-E_r/k\theta}.$$

Here, C contains ν^4 as a factor but is otherwise practically constant for a given band, $\varepsilon^{-E_r/k\theta}$ is a Boltzmann factor giving the distribution of molecules in the initial state, while i, the "*intensity factor*," is proportional to the probability of transition and to the statistical weight of the initial level. The Boltzmann factor depends on the conditions of excitation; for thermal equilibrium θ is the absolute temperature: in other cases it is the "*effective temperature*" chosen to fit the intensity distribution. Under special conditions of excitation a different function may be necessary. This factor is the same for all lines having the same initial state and its main effect is to give the fading out of the lines of the branches with increasing value of K. The intensity factor i is of more interest here as it depends on the values of Λ and is different for the different branches. Thus a study of the relative intensities of the lines of the different branches gives an additional check on the classification of the transition. The values of i for the transition ${}^1\Pi \rightarrow {}^1\Delta$ are:—

$$\text{P(K).} \qquad i = \frac{(\text{K} + \Lambda)(\text{K} + \Lambda - 1)}{\text{K}}$$

$$\text{Q(K).} \qquad i = \frac{(2\text{K} + 1)(\text{K} + \Lambda)(\text{K} - \Lambda + 1)}{\text{K}(\text{K} + 1)}$$

$$\text{R(K).} \qquad i = \frac{(\text{K} - \Lambda)(\text{K} - \Lambda + 1)}{\text{K}}$$

where K is the larger of K′ and K″ and Λ the larger of Λ' and Λ''.

The values of i for the first few members of the branches are given in Table IV.

Table IV.—Intensity Factors.

K.	R Branch. $i = \frac{(\text{K}-2)(\text{K}-1)}{\text{K}}$.	Q Branch. $i = \frac{(2\text{K}+1)(\text{K}+2)(\text{K}-1)}{\text{K}(\text{K}+1)}$.	P Branch. $i = \frac{(\text{K}+2)(\text{K}+1)}{\text{K}}$.
2	0·6	3·3	6·0
3	1·5	5·8	6·6
4	2·4	8·1	7·5
5	3·3	10·2	8·4

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* *Cf.* Ruark and Urey, "Atoms, Molecules and Quanta," pp. 697–698. McGraw Hill (1930).

It is to be noticed that the effect of *i* is to give the P branch lines nearly equal to the Q branch lines, while R branch lines are much weaker.* This is quite different from the result obtained for $^1\Pi \rightarrow {}^1\Sigma$ transitions where the R and P branches are nearly equal in intensity while the Q branch is about twice as strong. The weakness of the R branch is very well brought out in the λ 3240 band. Figs. 2 and 3, Plate 2, show a photograph of the band and a microphotometer record, from which it will be seen that the distribution of intensity is in general agreement with Table IV. For higher values of K the Boltzmann factor becomes important, causing the intensities to decrease.

Correlation of Molecular and Atomic Energy Levels.

Mulliken† has considered the correlation of the molecular energy levels of NH with the lowest energy states of the "*united atom*," O, and with the lowest energy states of the N atom plus an unexcited H atom.‡ The predicted stable states derivable from combination of an unexcited H atom with an N atom in its lowest states ^4S, ^2D and ^2P are $^3\Sigma$ from ^4S, $^1\Delta$, $^3\Pi$ and $^1\Pi$ from ^2D and $^1\Sigma^+$ from ^2P. The $^3\Pi$ and $^3\Sigma$ levels may be identified with the initial and final levels of the λ 3360 band and the $^1\Pi$ and $^1\Delta$ levels with the initial and final levels of the λ 3240 band. This leaves the $^1\Sigma^+$ level as yet unidentified. Transitions from the $^1\Pi$ level to this level are to be expected but with the source used by the author it is difficult to find such a band on account of the large number of lines of the H_2 spectrum occupying its probable region. An attempt is being made to eliminate these.

Catalogue of Wave-lengths.

In Table V is given a catalogue of wave-lengths, wave-numbers and classification of the lines measured. After the wave-lengths numbers representing the order of intensities on a scale of 10 are given in parentheses. These are not to be taken as *proportional* to the intensity since they are obtained from

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* In the case of the reverse transition $^1\Delta \rightarrow {}^1\Pi$, the effect of *i* is to give a much weaker P branch while the Q and R branches are nearly equal in strength. This is illustrated in Jevons's Report, *loc. cit.*, fig. 34 (c), p. 135. The diagram also includes the effect of the Boltzmann factor calculated for thermal equilibrium at about 1000° Abs.

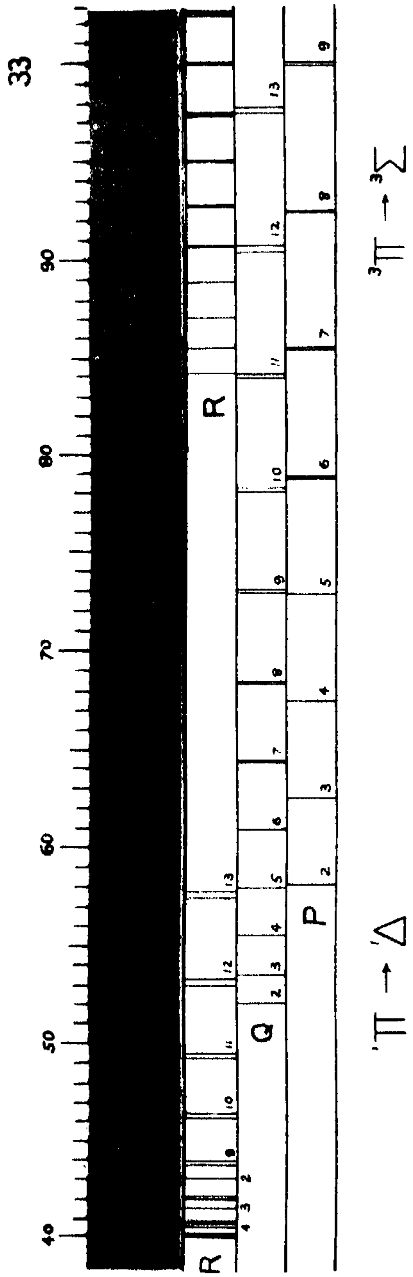
† 'Rev. Mod. Phy.,' vol. 4, p. 6 (1932).

‡ The variation of the energy of the levels with respect to the internuclear distance is considered. The "united atom" represents one limit where the internuclear distance is zero, the two separate atoms N and H represent the other limit where the internuclear distance is infinite.

Table V.—Catalogue of Wave-lengths.

λ (*i*).	ν.	Classification.
3240·061 (6)	30854·74	R (5)
40·137 (8)	54·02	R (5); R (6)
40·235 (6)	53·08	R (6)
40·526 (6)	50·31	R (4)
40·580 (6)	49·80	R (4)
40·759 (6)	48·10	R (7)
40·882 (6)	46·93	R (7)
41·520 (5)	40·85	R (3)
41·542 (5)	40·64	R (3)
41·957 (4)	36·70	R (8)
42·107 (5)	35·27	R (8)
43·023 (3)	26·56	R (2)
43·731 (4)	19·83	R (9)
43·924 (5)	18·00	R (9)
46·132 (3)	30797·04	R (10)
46·358 (4)	94·89	R (10)
49·162 (3)	68·32	R (11)
49·432 (3)	65·76	R (11)
51·950 (9)	41·94	Q (2)
52·872 (2)	33·23	R (12)
53·179 (2)	30730·33	R (12)
53·414 (10)	28·11	Q (3)
55·352 (10)	09·81	Q (4)
55·388 (10)	09·47	Q (4)
57·806 (10)	30686·68	Q (5)
57·858 (10)	86·20	Q (5)
57·940 (10)	85·42	P (2)
60·762 (9)	58·86	Q (6)
60·334 (9)	58·19	Q (6)
62·397 (9)	43·50	P (3)
64·251 (8)	26·09	Q (7)
64·346 (9)	25·20	Q (7)
67·350 (9)	30597·05	P (4)
68·275 (8)	88·39	Q (8)
68·398 (8)	87·24	Q (8)
72·792 (10)	46·16	P (5)
72·845 (10)	45·68	Q (9); P (5)
73·011 (8)	44·13	Q (9)
78·013 (7)	30497·52	Q (10)
78·206 (7)	95·73	Q (10)
78·732 (9)	90·83	P (6)
78·788 (9)	90·30	P (6)
83·771 (6)	44·03	Q (11)
83·991 (8)*	42·01	Q (11)
85·192 (9)	30·88	P (7)
85·264 (9)	30·22	P (7)
90·158 (6)	30384·96	Q (12)
90·433 (9)*	82·42	Q (12)
92·172 (7)	66·37	P (8)
92·274 (8)	65·43	P (8)
97·176 (9)*	20·29	Q (13)
97·511 (6)	17·20	Q (13)
99·545 (9)	30298·51	P (9)
99·677 (9)*	97·31	P (9)

* Lines not resolved by the microphotometer.


33
32
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60
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R
Q
P
$^3\Pi \rightarrow {}^3\Sigma$
$^1\Pi \rightarrow {}^1\Delta$

Fig.2.

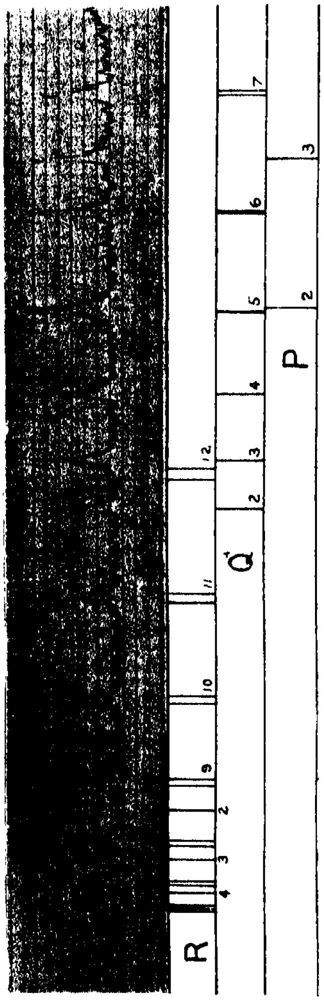
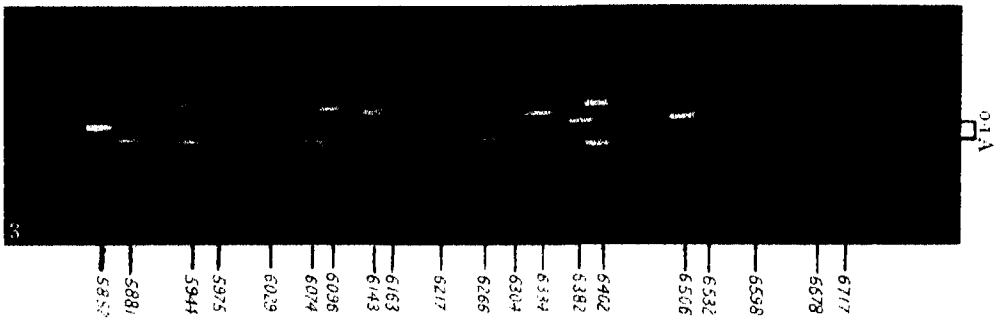

R
Q
P

Fig.3.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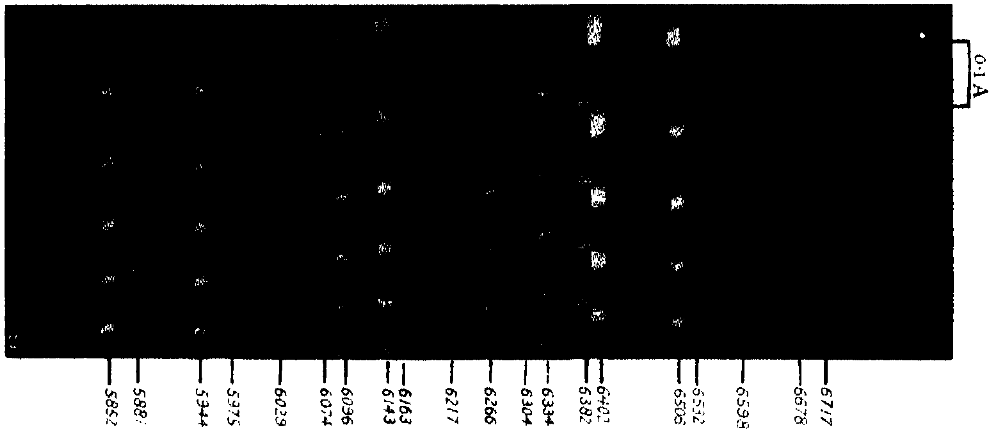
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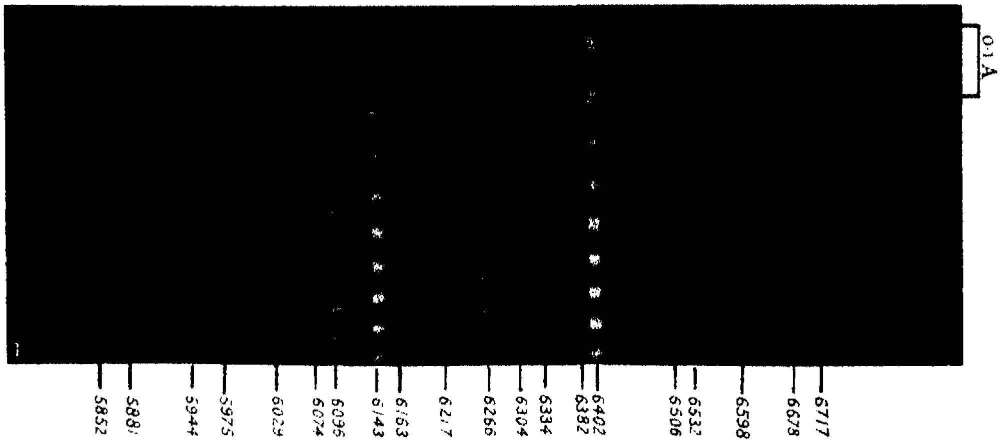
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(*Facing p.* 123.)

uncorrected ordinates of the microphotometer trace. They allow, however, a more finely divided scale than eye-estimates and a more accurate correlation of widely separated lines.

Acknowledgments.

The author is greatly indebted to the Commonwealth Fund for a Fellowship in Physics during the tenure of which this work was carried out. The author also wishes to thank Professor T. R. Birge and Associate Professor F. A. Jenkins for hospitality and assistance at the spectroscopic laboratory of the University of California.

Summary.

(1) A band at λ 3240 was observed near the λ 3360 band of NH in the spectrum of a heavy-current discharge tube containing nitrogen and hydrogen. Its occurrence in other sources containing nitrogen and hydrogen was investigated. It is also attributed to NH.

(2) The band was photographed under high dispersion. Analysis showed that the band possessed the intensity distribution and number of "missing lines" characteristic of a $^1\Pi \rightarrow {}^1\Delta$ transition. The narrow doubling occurring in each of the P, Q and R branches is attributed to Λ-doubling of the $^1\Pi$-levels.

(3) The rotational term differences are obtained and values of the rotational constants calculated.

(4) The relation of the electronic levels of the molecule NH to the lowest levels of the atom N is discussed.

(5) A catalogue of wave-lengths is given.

DESCRIPTION OF PLATE.

Fig. 2.—Enlargement of the λ 3240 band of NH from a plate taken with the second order of a 21-foot grating. Part of the R-branch of the λ 3360 band is shown on the right. Note the weakness of the R-branch of the λ 3240 band and the gap of four lines in the continuity of the P and R branches through the origin.

Fig. 3.—Zeiss microphotometer trace of part of the λ 3240 band near the origin.

Wave-lengths of the Red Lines of Neon and their Use as Secondary Standards.

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(Communicated by A. Fowler, F.R.S.—Received July 15, 1933.)

[PLATE 3.]

Introduction.

The spectrum of neon is dominated by a strong group of lines in the red. These are easily produced in an ordinary Geissler tube with very great intensity, and are sufficiently sharp to give measurable interference fringes with long path differences, of 120,000 waves or so.

For these reasons the red lines of neon appear to be eminently suitable for use as secondary standards, and in view of the good agreement of the wave-length determinations of a number of observers (especially Burns, Meggers, and Merrill at the Bureau of Standards) they were adopted as secondary standards by the International Astronomical Union in 1922.

A few years later it was discovered that each of the lines is accompanied by a weak satellite about 20 mA. to the violet of the main line. Also, under certain conditions, the lines could be made to show self-reversal, although under normal conditions of observations they are quite free from this defect. This led Buisson and Jausseran,* and Nagaoka† to throw doubt on the suitability of the neon lines for use as secondary standards.

However, the lines appeared to be very accurate as standards in actual use, and a preliminary investigation of the neon scale which was carried out as a check on the accuracy of my measurements of the violet krypton lines indicated that, when measured with instruments of high resolving power, the neon wave-lengths are free from any systematic error greater than one- or two-tenths of a mA.

In order to determine definitely whether the neon lines may be used as secondary standards, I have now made a large number of direct comparisons with the primary standard. The results are presented in this paper. They confirm the preliminary result so far as observations with apparatus of high resolving power (over about 250,000) are concerned, and are in better agreement with the Bureau of Standards' wave-lengths* than with the I.A.U. adopted values. But it was found that with low resolving powers the wave-lengths become systematically lower, till a minimum is reached at about 100,000, after which no further change in the apparent wave-lengths takes place. The wave-lengths at high resolving power correspond to the main component alone, while those at low resolving powers correspond to the centres of gravity of the unresolved blends. From the data obtained with interferometers of low resolving power, a table has been made giving the necessary corrections to be applied when the neon lines are used as standards with such apparatus. These corrections are quite small, the amount being only about 2 mA. even with apparatus of the lowest resolving power. They are accurate to $\pm 0 \cdot 001$ A., which is about the limit of accuracy attainable with low resolving power étalons.

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* 'Rev. Optique.,' vol. 5, p. 149 (1925).

† 'Proc. Imp. Acad.,' vol. 8, p. 231 (1932).

It thus seems quite possible to use the neon lines as accurate secondary standards. It is, of course, essential to use a discharge tube free from self-reversal, but this presents no difficulty. Suitable conditions for exciting the lines are stated in the paper.

All the observations in this investigation were made on the spectrum of ordinary atmospheric neon, which has only one part in ten of the heavier isotope, and the results naturally only apply to this kind of neon. It is necessary to mention this point because the isotopes of neon can now be separated by fractional diffusion and it is possible to prepare neon in which the Ne 22 lines are as strong as the Ne 20 lines.

Experimental.

The observations were made with the identical apparatus used for the previous work† on krypton, so no further description of it need be given here. In all cases, however, fixed étalons of fused silica were used. The temperaure of the equable temperature room, in which the observations were made, remained constant to within one- or two-hundredths of a degree during the course of a comparison, so that there was no trouble on account of change of length of the étalons due to expansion.

A very efficient heat-insulated furnace was made by Messrs. Catterson, Smith & Co. for the purpose of heating the cadmium tube to 320° C., and this was of great assistance in keeping the temperature of the room constant.

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* The eight figure means given by Burns, 'J. Opt. Soc. Amer.,' vol. 2 (1925).

† C. V. Jackson, 'Proc. Roy. Soc.,' A, vol. 138, p. 148 (1932).

The cadmium lamps were of the type used by Michelson and were excited by a small transformer, which was also used for exciting the neon tubes. The current for the cadmium tubes was 10 mA., while a current of 15–20 mA. was normally used for the neon tubes, which were always observed transversely. Neon tubes filled at pressures ranging from 5 to 15 mm. Hg were found to give results identical within the experimental error. The bore of all the capillary tubes was 1·25 mm., and the electrodes were of aluminium or magnesium. The neon was carefully purified from the active gases. Even with currents up to 100 mA. the neon lines are free from self-reversal under these condition, as shown by the photographs reproduced in Plate 3.

In most cases the new Ilford Hypersensitive plates were used. They were entirely satisfactory and their extreme sensitivity in the region 5800–6500 enabled the neon lines to be photographed in about 2 minutes, while a similar exposure sufficed for the red line of cadmium.

Observations were made with interferometer plates coated with sputtered or evaporated silver, or sputtered platinum. The thickness of the separators used ranged from 2·5 mm. to 30 mm. In all about 70 direct comparisons with the primary standard were made.

On account of the apparent change in wave-lengths of the neon lines when observed with thin interferometers, the phase correction of the plates was determined with the aid of krypton lines. This correction is very small, even with the shortest étalons, because the neon lines are in nearly the same spectral region as the primary standard.

The wave-lengths are given for air at 15° C. and 760 mm., and 50% humidity. The correction to dry air is less than 0·0001 A. and was not worth while applying, while the other corrections were never more than 0·0001 A.

The wave-lengths obtained with interferometers of high resolving power are given in Table I and discussed in paragraph (*a*), while those obtained with lower resolving powers are given in Table III and discussed in paragraph (*b*).

(*a*) *The Wave-lengths of the Neon Lines with Interferometers of High Resolving Power.*—Twenty-eight plates were taken with four different interferometers, whose resolving power lay between 250,000 and 800,000. The results of the measurements of these plates are given in Table I. At the head of each column is given a brief description of the interferometer used, and at the foot of each column is given the number of plates measured. The first column contains the whole number of the wave-length, while the next four columns contain the decimal places. The sixth column gives the weighted mean of these.

It can be seen from Table I that there is clearly no systematic difference between the four series, greater than the experimental accuracy, about 0·0001 A. for systematic errors. The lines can therefore be considered as definitely suitable for use as secondary standards in these conditions.

Table I.—Wave-lengths of Neon Lines when observed with étalons of High Resolving Power.

Film gap R.P.	Silver 1 cm. 280,000.	Platinum 2 cm. 350,000.	Platinum 3 cm. 500,000.	Silver 3 cm. 800,000.	Mean.	ν.	Terms.
5852	4877	4878	4877	4874	4876	17082·0275	$2s_2-2p_1$
5881	8950	8944	8949	8948	8948	16996·6247	$2s_5-2p_2$
5944	8343	8340	8340	8345	8343	16816·6784	$2s_5-2p_4$
5975	(535*)	5339	5340	(5334*)	5340	16730·2826	$2s_5-2p_5$
6029	(997*)	9976	9974	(997*)	9973	16579·1749	$2s_4-2p_2$
6074	3379	3379	3374	3378	3377	16458·1539	$2s_4-2p_3$
6096	1637	1629	1629	1630	1630	16399·2313	$2s_4-2p_4$
6143	0623	0624	0620	0613	0620	16274·0327	$2s_5-2p_6$
6163	5944	5942	5940	5939	5941	16219·8213	$2s_3-2p_2$
6217	2813	2818	2814	2812	2814	16079·7613	$2s_5-2p_7$
6266	4953	4954	4946	4948	4949	15953·4810	$2s_3-2p_5$
6304	-	7893	7892	7893	7893	15856·5824	$2s_4-2p_6$
6334	4282	4283	4279	4280	4280	15782·3904	$2s_5-2p_8$
6382	9914	9912	9915	9915	9915	15662·3145	$2s_4-2p_7$
6402†	2461	2460	2461	2462	2461	15615·2107	$2s_5-2p_9$
6506	5279	5277	5279	5284	5280	15364·9434	$2s_4-2p_8$
6532	—	8827	8823	8823	8824	15302·9598	$2s_2-2p_7$
6598	—	9527	9528	9534	9530	15149·7443	$2s_2-2p_2$
6678	—	2768	...	2764	2766	14969·7980	$2s_2-2p_4$
6717	—	-	0427*	..	0427	14883·4031	$2s_2-2p_5$
No. of plates	5	5	12	6	28	—	....

* Measured on two plates only with these étalons.

† This line is somewhat broader than the other neon lines.

The last column but one contains the wave-numbers *in vacuo* corresponding with the mean wave-lengths. These were found by reducing the wave-lengths to vacuum with the aid of Meggers and Peters' data as given in the last columns of Kayser's "Tabelle der Schwingenszahlen." The reciprocals of these vacuum wave-lengths were divided out on a calculating machine.

Since the neon lines measured in this investigation have all been classified into a $2s-2p$ multiplet, it is possible to use them for deriving term values. Assuming $2s_2 = 38821\cdot1000$, the following values were found :—

$2s_2$	38821·1000	$2p_1$	21739·0725	$2p_6$	24393·9488
$2s_3$	39891·1778	$2p_2$	23671·3565	$2p_7$	24588·2183
$2s_4$	40250·5326	$2p_3$	23792·3787	$2p_8$	24885·5894
$2s_5$	40667·9800	$2p_4$	23851·3016	$2p_9$	25052·7693
		$2p_5$	23937·6971	($2p_{10}$	26452·024*)

From these term values it is possible to calculate the relative wave-lengths of the lines. This calculation naturally introduces any error in the refractive index of air, as measured by Meggers and Peters; but this is not likely to have any very serious effect even in the fourth decimal place of the wave-lengths, because the lines occupy so small a spectral region.

These calculated wave-lengths together with the observed values are given in Table II. The agreement is quite satisfactory, the average difference being only ± 0·0002 A. The observed and calculated values found at the Bureau of Standards by Burns, Meggers and Merrill are given in the third and fourth columns, for comparison. It can be seen that the two sets of observed wave-lengths are in very good agreement, the mean accidental difference being ± 0·0002 A., while the systematic difference is well under 0·0001 A. The agreement between the two sets of calculated wave-lengths is nearly as good. The observations of Burns, Meggers and Merrill are strictly comparable with the present high resolving power wave-lengths because they also were made with interferometers of high resolving power on neon tubes completely free from self-reversal. The average difference between their observed and computed wave-lengths is also about ± 0·0002 A.

Since the two sets of observed wave-lengths appear to be of about the same degree of accuracy, the mean of the two is given in the fifth column of Table II. The average difference between the wave-lengths in this column and the two sets of observed values is only ± 0·0001 A. It is significant also that with either set of calculated wave-lengths the residuals are smaller when the mean values in the fifth column are used for comparison than when the respective observed wave-lengths are so used. This seems to indicate that a definite increase in accuracy is attained by taking the mean of the two observed wave-lengths.

In both cases, however, the residuals are appreciably greater for the calculated than for the observed wave-lengths. The lower accuracy of the calculated wave-lengths may be due to errors in the vacuum corrections. It is not due to an intensity equation in either series of observed wave-lengths.

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* Calculated from 7032·414, measured on two 3 cm. Pt plates only.

Measurements of the wave-lengths of the neon lines have also been made by Meissner,[*] Priest,[†] Monk,[‡] Wallerath,[§] and Babcock[||], but these were only given to three places of decimals. They all appear to refer to the high resolving power wave-lengths and are in good agreement with the eight figure values found by Burns, Meggers and Merrill, and in this investigation. Meissner and Wallerath used a vacuum arc for producing the red line, instead of the correct

Table II.—Comparison of Observed and Calculated Wave-lengths of Neon Lines when observed with High Resolving Power.

	Jackson.		Bureau of Standards.		Mean of Bur. Stand. obs. and Jackson obs.
	Observed.	Calculated.	Observed.	Calculated.	
5852	4876	4876	4880	4879	4878
5881	8948	8951	8954	8954	8951
5944	8343	8343	8343	8342	8343
5975	5340	5339	5340	5339	5340
6029	9973	9969	9972	9970	9972
6074	3377	3377	3377	—	3377
6096	1630	1631	1630	1631	1630
6143	0620	0625	0624	0629	0622
6163	5941	5941	5944	5943	5942
6217	2814	2813	2807	2809	2811
6266	4949	4950	4950	4954	4950
6304	7893	—	7893	7892	7893
6334	4280	4279	4280	4278	4280
6382	9915	9916	9913	9915	9914
6402	2461	2461	2455	2455	2458
6506	5280	5281	5278	5281	5279
6532	8824	8825	8827	8823	8826
6598	9530	9528	9528	9529	9529
6678	2766	2764	2760	2760	2762
6717	0427	0428	0427	0428	0427

Mean residuals :—

Jackson observed—Calculated	±0·0002 A.
Bur. Stand. observed—Calculated	±0·0002 A.
Bur. Stand. observed—Jackson observed	±0·0002 A.
Bur. Stand. observed—Mean observed	±0·0001 A.
Jackson observed—Mean observed	±0·0001 A.

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[*] 'Ann. Physik,' vol. 51, p. 115 (1916); and 'Phys. Z.,' vol. 17, p. 549 (1916).

[†] 'Bull. Bur. Stds.,' vol. 6, p. 573 (1911).

[‡] 'Astrophys. J.,' vol. 62, p. 375 (1925).

[§] 'Ann. Physik,' vol. 75, p. 37 (1924).

[||] 'Astrophys. J.,' vol. 66, p. 256 (1927).

source. The neon tubes used by Wallerath and Babcock were entirely different from those used in this and the other investigations.

The value 5852·4875 which was found in 1931* was obtained with high resolving power, using a Hilger G.E.C. neon lamp as light source. Observations on the other lines showed that they were identical in wave-length with those emitted by a Geissler tube to an accuracy of about 1 in 15 million. This is in agreement with the observations of Wallerath and Babcock, who also used lamps of the G.E.C. type. It is therefore quite safe to use this convenient source unless the very highest accuracy is required; but the lines 6402 and 6143 should not be used with this source as Babcock found that they were reversed in one or two of his lamps. They were not reversed in any of the four lamps which I have used, but 6402 was broadened in all of them.

(*b*) *The Wave-lengths of the Neon Lines with Interferometers of Resolving Power less than* 250,000.—Since each of the neon lines is accompanied by a faint satellite on the violet side, it seems very probable that when the resolving power of the interferometer is inadequate to separate the main line and its satellite, the resulting wave-lengths will be shorter than those obtained with apparatus sufficiently powerful to resolve the main line completely. In the limiting case of low resolving power the resulting wave-length will be that of the centre of gravity of the line and its satellite. This can be calculated from the known wave-lengths for high resolving power and the known separations of the main lines and the satellites, but it is impossible to calculate the apparent wave-lengths of the blends with intermediate resolving power. The only simple way of solving this problem is to make a series of direct measurements of the apparent wave-lengths with low and intermediate resolving powers.

Accordingly I made a series of measurements of the wave-lengths of the neon lines, using interferometers ranging in resolving power from 70,000 to 180,000, by direct comparison with the red line of cadmium. Separations of $\frac{1}{4}$, $\frac{1}{2}$ and 1 cm. were used, and the plates sputtered either with thin silver or thin platinum. The results of these comparisons are given in Table III. At the head of each column is given a description of the interferometer used and also its approximate resolving power. This was determined by finding the smallest fraction of an order of interference by which lines may differ and still be resolved. This fraction, which was about one-fifth for thin platinum and one-eighth or one-tenth for thin silver, for the red part of the spectrum, is divided into the order of interference to give the resolving power.

In Table III the first column contains the observed wave-length for high resolving power. The next four columns contain the wave-lengths obtained with the interferometer stated at the head of the column. Each of these wave-lengths is followed by δλ, the difference in milliangstroms between it and the wave-length given in the first column. In the sixth column is given the wave-length found by Pérard* with a Michelson interferometer of short path difference (very low resolving power).

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* C. V. Jackson, 'Proc. Roy. Soc.,' A, vol. 133 p. 562 (1931).

Table III.—Wave-lengths of Neon Lines when observed with Resolving Powers under 250,000.

λ	Ag ¼ cm. 70,000.	δλ. mA.	Pt ½ cm. 90,000.	δλ. mA.	Ag ½ cm. 140,000	δλ. mA.	Pt 1 cm. 180,000.	δλ. mA.	Pérard.	δλ. mA.	δλ mA. calculated for blend.
5852·4878	487	−0·8	0·485	−2·8	4844	−3·2	4865	−1·3	4840	−3·8	2·7
5881·8951	894	−1·1	0·894	−1·1	8947	−0·4	8942	−0·9	8910	−4·1	2·0
5944·8343	831	−3·3	0·832	−2·3	8327	−1·6	8324	−1·7	8300	−4·3	2·0
5975·5340	530	−4·0	0·531	−3·0	5326	−1·4	5341	+0·1	—		2·1
6029·9973	995	−2·3	0·995	−2·3	9960	−1·3	9966	−0·7	—		2·1
6074·3377	335	−2·7	0·335	−2·7	3358	−1·9	3365	−1·2	—		2·1
6096·1630	161	−2·0	0·160	−3·0	1615	−1·5	1626	−0·4	1600	−3·0	2·1
6143·0622	061	−1·2	0·060	−2·2	0602	−2·0	0613	−0·9	—		2·1
6163·5942	591	−3·2	0·591	−3·2	5935	−0·7	5934	−0·8	—		2·1
6217·2814	278	−3·0	0·279	−2·0	2814	±0·0	2811	−0·3	—		2·1
6266·4950	491	−4·0	0·492	−3·0	4932	−1·8	4949	−0·1	—		2·2
6304·7893	788	−1·3	0·787	−2·3	7880	−1·3	7886	−0·7	—		2·2
6334·4280	427	−1·0	0·426	−2·0	4259	−2·1	4275	−0·5	—		2·2
6382·9914	989	−2·4	0·989	−2·4	9893	−2·1	9911	−0·3	—		2·2
6402·2458	244	−1·8	0·243	−2·8	2640	−1·8	2449	−0·9	2460	+0·2	2·2
6506·5279	526	−1·9	0·525	−2·9	5253	−2·6	5271	−0·8	—		2·3
6532·8826	880	−2·6	0·879	−3·6	8804	−2·2	8820	−0·6	—		2·3
6598·9529	951	−1·9	0·950	−2·9	9500	−2·9	9520	−0·9	—		3·1
6678·2762	274	−2·2	0·273	−3·2	2732	−3·0	2752	−1·0	—		3·1
6717·0427	040	−2·7	0·039	−3·7	0407	−2·0	0420	−0·7	—		3·1
Mean δλ		−2·3 mA.		−2·6 mA.		−1·8 mA.		−0·7 mA.		−3·0 mA.	−2·3 mA.
No. of plates	8		17		10		5				
Probable systematic error	±0·002 A.		±0·001 A.		±0·0007 A.		±0·0004 A.				

At the foot of each column are given the appropriate figures for the mean value of δλ, the number of plates on which the lines were measured, and the greatest likely systematic error for each series of wave-lengths.

The seventh column contains the values of δλ for the limit of low resolving power, calculated on the assumption that the wave-length of the line under these conditions is that of the centre of gravity of the blend of the strong line (due to Ne 20) and the weak line (due to Ne 22). It is also assumed that the high resolving power wave-lengths are those of the strong lines of Ne 20. The data of Nagaoka* were used for the doublet separation, and it was assumed that if no self-absorption occurs the ratio of the intensities of the lines is 10 to 1, *i.e.*, that of the abundance of the isotopes.

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* 'C. R. Acad. Sci. Paris,' vol. 176, p. 375 (1923).

In fig. 1 the observed mean values of $\delta\lambda$ are plotted against the resolving power and indicated by circles. The crosses are values of $\delta\lambda$ calculated as indicated above on the assumption that with resolving power less than 100,000 complete blending of the main line and the satellite takes place, while with resolving power over 300,000 it is assumed that resolution is complete. It is noteworthy that the points are all in very good agreement; this proves that there can be no appreciable self-reversal, for if there were the observed $\delta\lambda$'s would be greater than those calculated from Nagaoka's doublet separations.

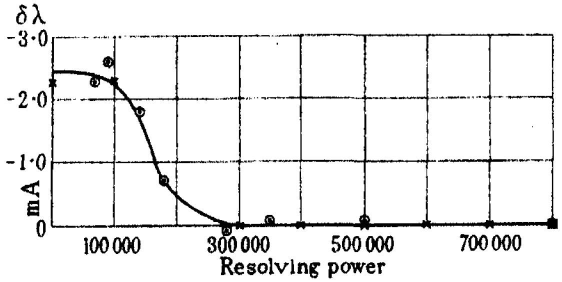

Fig. 1.

The values of $\delta\lambda$ obtained from this curve may be used to construct a table giving the mean correction necessary to reduce the wave-lengths of neon observed at high resolving power to their apparent wave-lengths at low and medium resolving powers.

These corrections are given in Table IV. They are quite small and if they are applied the neon wave-lengths may be relied upon as accurate secondary standards with all types of apparatus. The correction is definitely a function of the resolving power of the interferometer, not of its thickness, and is therefore presumably applicable also to wave-length measurements with grating or prism spectrographs. The greatest probable error of the corrections is given in the third column.

Although, strictly speaking, the corrections are not the same for all the neon lines at a given resolving power, no sensible error is introduced by applying a mean correction to all the lines. In any case this would only affect the relative values of the neon lines, without introducing any scale error into the unknown wave-lengths being compared with neon. It is because the $\delta\lambda$'s are so nearly the same for all the neon lines that Burns could detect no systematic variations of the wave-lengths with different resolving powers in his measurements made at the Allegheny Observatory. As Burns clearly states in his paper, this work concerned only the relative values of the neon lines and had no bearing on their absolute wave-lengths.

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* 'Proc. Imp. Acad. Tokyo,' vol. 8, p. 231 (1932).

With an interferometer separation of 7 or 8 cm. the satellite becomes superposed on the next lower order of the main line, and is liable to change the wave-length by about two- or three-tenths of a milliangstrom. This occurrence does not, however, need serious consideration as the neon lines are too broad for use with plate separations of more than 5 cm.

Table IV.—Mean Corrections to be applied to the High Resolving Power Wave-lengths of the Neon Red Lines when they are observed with Resolving Powers under 250,000.

Resolving power.	Mean correction.
0 to 100,000	− 2·3 mA. ± 0·001 A.
100,000 to 120,000	− 2·1 mA. ± 0·001 A.
120,000 to 140,000	− 1·8 mA. ± 0·001 A.
140,000 to 160,000	− 1·5 mA. ± 0·001 A.
160,000 to 170,000	− 1·0 mA. ± 0·0007 A.
170,000 to 180,000	− 0·8 mA. ± 0·0005 A.
180,000 to 200,000	− 0·6 mA. ± 0·0005 A.
200,000 to 240,000	− 0·3 mA. ± 0·0005 A.
240,000 to 280,000	− 0·1 mA. ± 0·0003 A.
Over 280,000	Nil

(*c*) *Conditions for Excitation of the Neon Lines.*—In this investigation it was found that the red neon lines were quite free from self-reversal when excited with currents between 10 and 40 mA., and that within this range there was no detectable difference in the wave-lengths obtained with different currents.

It was also found that tubes filled at 5 mm. pressure and those filled at 15 mm. pressure, gave results identical, within the experimental error. A systematic change of 0·0001 A. could have been detected. In this connection it may be added that Burns found no difference greater than 1 part in 16 million between the wave-lengths given by tubes filled at pressures between a fraction of a millimetre and several centimetres.

Burns, Meggers and Merrill used Geissler tubes having a capillary of 2½ mm. bore, and found the lines quite free from self-reversal with currents up to 50 mA. As is shown earlier in the paper their wave-lengths and mine agree within experimental error.

It is clearly not necessary to lay down any very stringent specifications for the method of exciting the neon lines, even when they are to be used as secondary standards of the highest accuracy. It is suggested that the following specification is adequate :—

(1) Pressure of neon not to exceed 15 mm. Hg.

(2) The bore of the capillary should be between 1 and 2½ mm.

(3) The current should not exceed 40 mA.

(4) The discharge tube should be of the ordinary Geissler type, viewed transversely.

In conclusion it is a great pleasure to the author to express his gratitude to Professor A. Fowler for his great interest and encouragement throughout the course of the work.

Summary.

(1) The wave-lengths of the red lines of neon have been compared with the primary standard, by means of Fabry-Perot interferometers of resolving powers ranging from 70,000 to 800,000. In all about seventy plates were measured.

(2) It was found that with resolving powers greater than about 250,000, the neon lines have constant wave-lengths, and the values found in this investigation are in almost perfect agreement with those of Burns, Meggers and Merrill. The systematic difference is under 0·0001 A., while the mean accidental difference is ± 0·0002 A.

(3) With lower resolving powers the apparent wave-lengths of the neon lines become systematically lower until constant values are reached at about 100,000, these being about 2 mA. smaller than those found at high resolving powers. This is caused by blending of the weak satellite (due to Ne 22) with the main line. It is shown that the observed changes in apparent wave-length are in good agreement with those calculated from the doublet separations given by Nagaoka.

(4) A table of corrections to be applied to the standard neon wave-lengths when they are used with apparatus of low resolving power is given. When these corrections are applied, the neon lines form satisfactory secondary standards for use with apparatus of low resolving power. The corrections are quite small and are accurate to within ± 0·001 A.

(5) The conditions for exciting the lines so that they are accurately reproducible in wave-length and free from self-reversal are given. The restrictions are not very stringent.

(6) The wave-lengths of the lines given by the Hilger-G.E.C. neon lamps do not differ from those given under the conditions described above by more than 1 part in about 15 million. If this lamp is used as a source of light, however, the lines 6402 and 6143 should not be used as standards as they appear reversed in some of the lamps.

DESCRIPTION OF PLATE (*facing p.* 123).

The spectrograms (1) and (2) were taken with a small two-prism spectrograph crossed with étalons of 2½ cm. and 1½ cm. gap. The plates were fairly heavily silvered and the resolving power was about 1,000,000 and 600,000 respectively.

For each an ordinary Geissler tube was observed transversely. The light was so intense that the exposure required was only 1 or 2 seconds. The current was 100 mA., and it can be seen quite clearly that there was no self-reversal.

The spectrogram (3) was taken by D. A. Jackson with a reflexion échelon crossed with a 10-foot quartz spectrograph. The resolving power was about 600,000. For this plate the neon was excited by high frequency current. The current was about 500 mA. and the bore of the tube was 7 mm. In this plate also it can be seen that the lines are quite free from self-reversal.

The Electrical Properties of Sea-Water for Alternating Currents.

By R. L. Smith-Rose, D.Sc., Ph.D. (The National Physical Laboratory).

(Communicated by E. V. Appleton, F.R.S.—Received July 31, 1933.)

1. *Introductory with Summary of Previous Work.*

In a recent communication the author* gave the results of an experimental investigation of the electrical properties of some samples of soil under alternating current conditions at frequencies from 100 to 10,000 kilocycles per second. It was considered desirable to carry out similar measurements on sea-water since this forms a large portion of the earth's surface over which electric waves are transmitted in the practice of radio communication. Taking sea-water as a typical electrolyte, a knowledge of its electrical properties is also of importance in connection with research in physical-chemistry.

The study of the properties of sea-water at radio-frequencies dates back to about 1906 when interest in this subject was aroused by the theoretical work of Sommerfeld and Zenneck on the propagation of electric waves over the earth's surface. The results of measurements at audio-frequencies on ninety samples of sea-water collected from the Mediterranean Ocean were published by Hill[*] in 1907. Similar conductivity measurements on water from the North Sea were described by Schmidt[†] in 1911, the mean value obtained at a temperature of 20° C. being $3 \cdot 6 \times 10^{10}$ e.s.u. (corresponding to a resistivity of 25 ohm-cm.). Uller[‡] pointed out that for the same salt-content and temperature, Hill's results for the Mediterranean gave a conductivity value about 65% higher than Schmidt's for the North Sea.

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* 'Proc. Roy. Soc.,' A, vol. 140, p. 359 (1933).

The first measurements at radio-frequencies appear to have been published by B. van der Pol,[§] who used a substitution method to compare the conductivity at a high frequency with the value at a power frequency of 90 cycles per second. The conductivity found in this manner for samples of sea-water taken near Hastings in the South of England was $3 \cdot 39 \times 10^{10}$ e.s.u. (resistivity 26·5 ohm-cm.) at a temperature of 12·5° C. Over a frequency range of 88 to 1100 kilocycles per second, the conductivity was found to be constant to within 0·5%. In a later communication, Rivers-Moore[‖] described a Kelvin double-bridge circuit arrangement devised for the purpose of making conductivity measurements on sea-water. Samples taken from Harwich Harbour on the East coast of England gave a conductivity of about $3 \cdot 4 \times 10^{10}$ e.s.u. (27 ohm-cm.) while for open sea-water off Weymouth[¶] on the South coast, a value of $3 \cdot 75 \times 10^{10}$ e.s.u. (24 ohm-cm.) was obtained, the temperature in each experiment being 15° C. This conductivity was found to be independent of frequencies up to the highest value employed of 100 kilocycles per second, and the value of its temperature coefficient was + 3% per degree Centigrade.

In the investigation of the electrical properties of soil at radio-frequencies, a certain amount of information has been gained in the past by measuring the attenuation of the field intensity of waves radiated overland, and comparing the experimental results with the theoretical values. For waves transmitted oversea, however, the attenuation on wave-lengths above 100 metres arising from currents set up in the sea-water is so small as to make it difficult to obtain reliable measurements. On the much shorter wave-lengths which are now in use for radio-communication, the absorption of energy by the sea-water may be more serious, but it is not easy to carry out field intensity measurements to an accuracy sufficient for the effect of the sea-water to be easily observed.

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[*] 'Proc. Roy. Soc. Edin.,' vol. 27, p. 233 (1907).

[†] 'Jahrb. Drahtl. Tel. u. Tel.,' vol. 4, p. 636 (1911).

[‡] 'Jahrb. Drahtl. Tel. u. Tel.,' vol. 4, p. 638 (1911).

[§] 'Phil. Mag.,' vol. 36, p. 88 (1918).

[‖] 'Electrician,' vol. 82, p. 174 (1919).

[¶] Drysdale, 'J. Inst. Elect. Eng.,' vol. 58, p. 590 (1920).

It therefore seems that laboratory measurements of the conductivity and dielectric constant are necessary in order that the effect of sea-water on the propagation of waves may be accurately determined over the whole range of frequencies in practical use. The object of the experiments now to be described was to supplement existing knowledge, particularly by increasing the frequency range of the measurements, and to obtain more definite information on the dielectric constant of the material.

2. *Method of Measurement and Preliminary Results.*

The method of measuring the electrical constants of sea-water is similar to that employed for the soil measurements (Smith-Rose, *loc. cit.*). The sample of water being measured is used as the dielectric in a condenser of suitable size and shape, and the effective capacitance and resistance of this condenser are measured by including it in a resonant circuit, which can be tuned through the working frequency. This circuit is coupled to a valve-maintained oscillating circuit, the reactance of which, and so the frequency generated, depends upon the tuning of the first circuit. As explained in the paper referred to, this arrangement provides a means of measuring the resistance and reactance of the condenser under test in terms of the frequency employed and the capacitance of the variable condenser in the tuned circuit.

Owing to the appreciably higher conductivity of sea-water it was necessary to employ smaller condensers for the samples than those used for the soil measurements. After a trial of various arrangements it was found convenient to use condensers formed of a straight piece of glass tube, 1 cm. internal diameter, fitted with platinum disc electrodes, 1 cm. in diameter, supported by corks at the ends of the tube. A series of such tubes was made so that the measurements could be carried out with condensers of various capacitances in air. The value of these air capacitances enter into the measurement of both the conductivity and dielectric constant of the material under examination; for the sample condensers made up, these capacitances were calculated from the dimensions. Although the sample condensers employed were not of the screened type, it was considered that the errors in measurement due to stray capacitances would be small on account of the high conductivity and dielectric constant of the material under examination. As in the soil investigation certain measurements were carried out at audio-frequencies with an ordinary capacitance bridge. The voltage applied to the condensers during the measurements was of the order 0·5 at radio-frequencies and 0·05 at audio-frequencies. The measured quantities did not appear to be sensitive to changes in these values in the ratio of 1 to 4.

Proceeding in the manner outlined above a number of preliminary measurements were carried out at several representative frequencies and with various dimensions of the condenser. A selection of the results obtained is given in Table I. As in the previous paper the values of dielectric constant and conductivity are in electrostatic units throughout.

Table I.

Frequency (kc./s.)	Length of cylindrical condenser (cm.)	Calculated capacitance of condenser (air dielectric) (C_0 $\mu\mu F$).	Condenser filled with sea-water.		Apparent values.	
			Capacitance ($\mu\mu F$).	Resistance (Ω).	Dielectric constant.	Conductivity (e.s.u.).
1·0	3·0	0·023	$0{\cdot}70 \times 10^{6}$	169	$30{\cdot}5 \times 10^{6}$	$2{\cdot}0 \times 10^{10}$
	6·2	0·011	$0{\cdot}30 \times 10^{6}$	227	27×10^{6}	$2{\cdot}1 \times 10^{10}$
	10·7	0·0064	$0{\cdot}11 \times 10^{6}$	333	17×10^{6}	$3{\cdot}7 \times 10^{10}$
100	3·0	0·023	300	81	13,000	$4{\cdot}3 \times 10^{10}$
	10·7	0·0064	20	276	3100	$4{\cdot}5 \times 10^{10}$
1200	3·0	0·023	13	79	570	$4{\cdot}3 \times 10^{10}$
	10·7	0·0064	10	275	1550	$4{\cdot}5 \times 10^{10}$
10,000	3·0	0·023	10	69	430	$5{\cdot}0 \times 10^{10}$
	10·7	0·0064	<1	260	<150	$4{\cdot}7 \times 10^{10}$

Several facts are illustrated by the results given in this table. In the first place, the apparent values of the dielectric constant and conductivity of sea-water, as derived directly from the measurements of the capacitance and resistance of the condenser containing the sample, vary with the length of the condenser employed. They are, therefore, not the true specific values of the quantities under investigation, but are in some way influenced by the dimensions of the container. It is next observed that the apparent dielectric constant, which has very large values at the audio-frequency of 1 kilocycle per second, decreases as the frequency is raised. At the highest frequency employed, viz., 10,000 kilocycles per second, the apparent value of the dielectric constant as determined with the largest container is less than 150; this limiting value is set by the difficulty of measuring the small effective capacitance (1 $\mu\mu F$) of the container in this instance. It may also be pointed out at this stage that the apparent value of the conductivity tends to increase with the frequency, although the variation, with either frequency or length of container, is not very large in the radio-frequency range.

3. *Discussion of Preliminary Results.*

In considering what is the true value of the dielectric constant of sea-water, it may be mentioned that most of the previous investigators have assumed that it plays a negligible part compared with the electrical conductivity. As Van der Pol (*loc. cit.*) showed, for example, if we assume that sea-water has the same dielectric constant as pure water, viz., about 80, and the conductivity is of the order 4×10^{20} e.s.u., the resistance of a typical condenser at a frequency of one million cycles per second is only one-thousandth of its parallel reactance. In terms of the expressions set down in the previous paper, we can neglect the dielectric constant, κ, in comparison with the conductivity σ, at any frequency, f, for which the quantity $\kappa f/2\sigma$ is small compared with unity. Assuming that $\kappa = 80$ and σ is about 4×10^{10} e.s.u., this condition is satisfied for all frequencies up to 10,000 kilocycles per second. Amongst the evidence which exists in support of the assumption that the dielectric constant of electrolytes is similar to that of water, reference may be made to some work published in America in 1930. A joint paper by Drake, Pierce and Dow* described measurements of the electrical constants of a very weak solution of potassium chloride (KCl) at high frequencies. Commencing with distilled water, the salt was added until a solution of 1/70 normal strength was obtained, without any change in the dielectric constant being perceptible, although the conductivity had increased two hundred times. A later paper by Lattey and Davies† describes measurements of the dielectric constant of weak solutions of four salts, including potassium and sodium chlorides, at frequencies from 4 to 8 kilocycles per second. Their results show that the presence of the salt in the water increases slightly the dielectric constant, the increase being proportional to the concentration. The total increase shown in their results is about 10%, *i.e.*, from 80 to 88. When, however, the concentration of the solution, and correspondingly its conductivity, is raised to the order given for sea-water in Table I, the dielectric constant appears to have abnormally high values at audio and at low radio-frequencies, and it would seem to be necessary to find some explanation of this effect.

It has previously been suggested that in order to explain these anomalies which are encountered in some solid dielectrics,‡ as well as in electrolytes, the sample of material with its electrodes may be represented as being equivalent to the circuit arrangement shown in fig. 1 (*a*). In this diagram, C_L and R_L are the capacitance and resistance values arising from the true dielectric constant and resistivity of the material, while C_{F_1}, C_{F_2} and R_{F_1}, R_{F_2} represent the effective capacitances and resistances of a polarization film formed during the passage of current at the contact surfaces between each electrode and the dielectric material. The equivalent effective capacitance and resistance of the cell will obviously depend upon the values of these individual components and the frequency employed. For analytical purposes the two films may be combined to form the circuit arrangement shown in fig. 1 (*b*). Since it has been shown from the measurements already made that for high radio-frequencies the dielectric constant is negligible in comparison with the conductivity the equivalent circuit may be still further simplified to that of fig. 1 (*c*), or alternatively to fig. 1 (*d*).

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* 'Phys. Rev.,' vol. 35, p. 613 (1930).

† 'Phil. Mag.,' vol. 12, p. 1111 (1931).

‡ *Cf.* Hartshorn, 'Proc. Phys. Soc.,' vol. 37, p. 215 (1925).

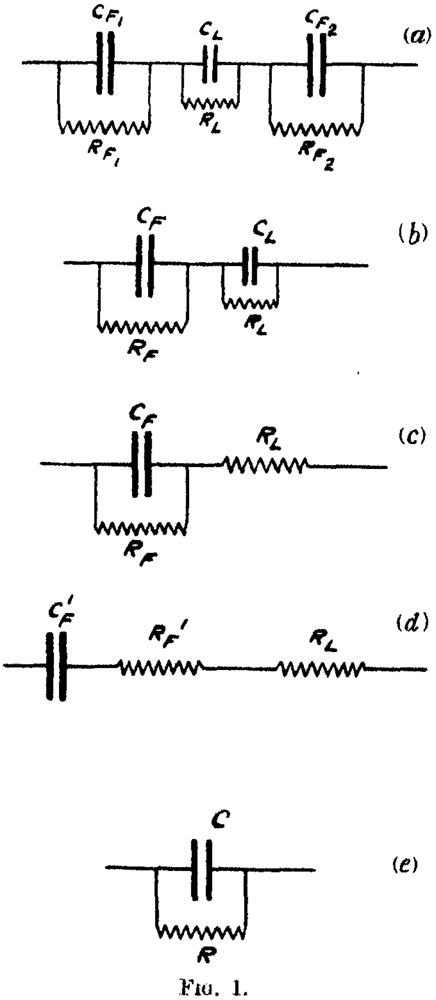

Fig. 1.

In carrying out the measurements the effective capacitance C and resistance R of the condenser containing the sea-water under examination, are obtained in terms of the parallel arrangement depicted in fig. 1 (*e*). If we equate the two circuit arrangements 1 (*c*) and 1 (*e*), we obtain the following relations between the various quantities involved :—

$$R_L + \frac{R_F}{1+(\omega C_F R_F)^2} = \frac{R}{1+(\omega C R)^2} \tag{1}$$

$$\frac{C_F R_F^2}{1+(\omega C_F R_F)^2} = \frac{C R^2}{1+(\omega C R)^2}\,. \tag{2}$$

The first equation involves three unknown quantities and in order to solve these from the data presented in Table I a first assumption may be made that for the frequency of 1 kilocycle per second the specific conductivity of the sea-water is equal to the mean value obtained at the radio-frequencies, *i.e.*, $4 \cdot 5 \times 10^{10}$ e.s.u. this value being independent of the length of the container. Employing this value to obtain R_L for insertion in equation (1), we can then solve equations (1) and (2) for the values of C_F and R_F. In this manner, it can be shown that for the three lengths of container employed in the measurements given in Table I at the frequency of 1 kilocycle per second, the value of the film capacitance, C_F, was about $1 \cdot 7$ μF while the resistance, R_F, was 260 ohms.

From the reasoning given above, it would appear that there is some justification for stating that the preliminary results given in Table I show that the conductivity of sea-water is nearly independent of frequency and that the dielectric constant is so small as to be negligible in comparison with this conductivity. The various anomalies shown in the table, viz., the very high apparent values of the dielectric constant, and the apparent variation with length of container of both the dielectric constant and the conductivity, can all be explained by assuming the existence of a film at the contact between each of the electrodes and the electrolyte, having a capacity of about $3 \cdot 4$ microfarads in parallel with a resistance of about 130 ohms.

4. *Further Measurements at Room Temperature.*

With the benefit of the experience gained in the preliminary tests described above a more complete series of measurements were carried out using three audio- and three radio-frequencies, and three lengths of container. These measurements were made at room temperature, which was recorded at the time, and corrections to the conductivity values were made in accordance with the temperature coefficient determined as described in the next section. The results of the measurements are given in Table II. It was observed during the course of the earlier work that when the condensers were first filled with the sea-water, the resistance values at audio-frequencies decreased appreciably during the first 10 minutes, after which they became approximately constant. It was considered that this was due to some chemical action between the sea-water and the electrodes, and to reduce the effect of this in the later measurements the platinum electrodes for the condensers were kept immersed in sea-water for a period of several days prior to the measurements.

At the higher radio-frequencies the capacitive reactance was so large compared with the resistance in parallel with it that it was not possible to make accurate measurements of the capacitance and even the values given in two cases for the frequency of 100 kilocycles per second must be regarded as only approximate. This fact is, in itself, evidence that at these frequencies the dielectric constant of the sea-water plays a negligible part in comparison with the conductivity.

Referring to the results given in Table II it will be seen that the measured values of capacitance and resistance are of the same order, although somewhat different in actual magnitude, as those obtained in the preliminary measurements. If the results taken at a frequency of 1 kilocycle per second are treated in the manner adopted in the previous section the values deduced for the film capacitance and resistance are about 4·7 microfarads and 100 ohms respectively.

Table II.

Length of cylindrical condenser. (cm.)	Temperature (° C.)	Frequency (kc./s.)	Measured values.		Calculated values.		Conductivity corrected to 20° C. (e.s.u.).
			C ($\mu\mu$F).	R (Ω)	C_F^1 (μF).	$R_F^1 + R_L$ (Ω).	
2·45	19	0·5	$1·75 \times 10^6$	100	7·5	77	$3·8 \times 10^{10}$
		1·0	$0·76 \times 10^6$	83	5·5	72	$4·0 \times 10^{10}$
		2·0	$0·30 \times 10^6$	78	3·7	72	$4·0 \times 10^{10}$
		100	220	75	2·1	75	$3·9 \times 10^{10}$
		1200	—	69	—	69	$4·2 \times 10^{10}$
		10,000	—	52	—	52	$5·6 \times 10^{10}$
10·4	19	0·5	$0·18 \times 10^6$	320	5·9	307	$4·0 \times 10^{10}$
		1·0	$0·06 \times 10^6$	290	5·0	286	$4·3 \times 10^{10}$
		2·0	$0·02 \times 10^6$	280	4·3	272	$4·5 \times 10^{10}$
		100	35	276	1·0	276	$4·5 \times 10^{10}$
		1200	—	276	—	276	$4·5 \times 10^{10}$
		10,000	—	250	—	250	$4·9 \times 10^{10}$
24·3	17·5	0·5	$0·031 \times 10^6$	760	6·1	755	$4·0 \times 10^{10}$
		1·0	$0·012 \times 10^6$	715	4·1	715	$4·2 \times 10^{10}$
		2·0	$0·006 \times 10^6$	690	2·2	685	$4·4 \times 10^{10}$
		100	—	690	—	690	$4·4 \times 10^{10}$
		1200	—	690	—	690	$4·4 \times 10^{10}$
		10,000	—	520	—	515	$5·8 \times 10^{10}$

The results given in columns 6 and 7 of Table II are those calculated for the equivalent circuit shown in fig. 1 (*d*), where the film is now represented by the capacitance C_F^1 and resistance R_F^1 in series. From a consideration of the film constants at any frequency on the basis of the analysis given in the previous section it can be shown that the value of $R_F{}^1$ is generally only about 5% or less of the values of $R_F{}^1 + R_L$. As this is scarcely outside the overall accuracy of the measurements, it will be sufficient for our purpose to take the values in column 7 of Table II as the resistance of the electrolyte in series with the capacitance of the electrode film given in column 6 of the table. On this basis the specific conductivity of sea-water has been calculated, and the results corrected to a uniform temperature of 20° C. are given in the last column. It will be noted that the values obtained in this manner are substantially independent of the length of the container, and we may therefore summarize the mean values as in Table III.

Table III.—Specific Conductivity of Sea-water at temperature of 20° C.

Frequency (kc./s.)	Conductivity (e.s.u. × 10^{10})
0·5	3·9
1·0	4·2
2·0	4·3
100	4·3
1200	4·3
10,000	5·4

The above measurements refer to samples of sea-water obtained near the Nab Tower in the English Channel; the salt content of these samples was found to be 3·8%.

The actual measured values in Table II are not considered to be accurate to much better than 5%, and the values given in Table III are the means of three sets of measurements,

From these results it appears that there is only a small increase of conductivity in proceeding from audio- to low radio-frequencies, but there is a marked increase of conductivity at the highest frequency of 10,000 kilocycles per second. Concerning the dielectric constant, it may be stated that, from the experiments and analysis given above, its value is so small that it plays a negligible part in comparison with the measured conductivity. The very high apparent values of dielectric constant obtained in measurements at audio-frequencies may be attributed to the effects of a polarization film capacitance having values such as those shown in the tables. It will be noticed in Table II that the capacitance of this film decreases as the frequency is raised, but, in any case, its effect becomes inappreciable at radio-frequencies. The constants of the film also vary appreciably with the state of the electrodes and their time of immersion in the liquid. It is considered to be outside the scope of this paper to study the formation and properties of this film in any further detail.

It has already been explained that if the dielectric constant of sea-water were the same as that of pure water, viz., 80, the condition of negligibility would be valid up to the highest frequencies here employed. As opportunity occurs it is proposed to extend the measurements to frequencies above 10,000 kilocycles per second, and it may then become possible to assess a more definite value to the dielectric constant of sea-water.

5. *Variation of Conductivity with Temperature.*

It has been seen from the results of previous investigators that the temperature coefficient of the conductivity of sea-water is quite considerable, about + 3% per ° C. This value is of the order commonly associated with the conductivity of electrolytes. It was considered desirable to extend the range of previous work by carrying out measurements of the conductivity by the method described in this paper. For this purpose, one of the sample condensers, 10·5 cm. long, was employed, filled with sea-water and placed in a water bath, the temperature of which could be varied over a suitable range. The resistance and capacitance of the condenser were measured at a single frequency of 1200 kilocycles per second, for various temperatures between 0° C. and 58° C. A second series of measurements was then made during which the water bath was cooled from the room temperature through 0° C. to a final temperature of − 12° C. At each temperature sufficient time was allowed for the contents of the condenser to acquire the temperature of the surrounding bath, and the measurements were repeated for conditions of rising temperature.

From all these measurements the conductivity of the sea-water was calculated and the results are shown in graphical form in fig. 2. It is seen that the conductivity value, which was $4 \cdot 3 \times 10^{10}$ e.s.u. at a temperature of 20° C., increases steadily to twice this value at about 60° C., and decreases to less than 3×10^{10} e.s.u. at 0° C. Over the range of temperature 0° C. to 40° C., the temperature coefficient of the conductivity is 2·7% per ° C. An interesting point to note in fig. 2 is the sudden decrease in conductivity at a temperature of about − 2° C., which is probably due to a change in constitution of the liquid on a partial separation of ice from the sea-water. This change took place quite suddenly, and there appeared to be no very well-defined hysteresis effect for conditions of rising and falling temperature, although control of the temperature to finer limits might have shown up such an effect. At temperatures from

— 3° to — 12° C., the temperature coefficient of the conductivity had a much lower value than that given above.

6. *Acknowledgments.*

The work described in the above paper was carried out as part of the programme of the Radio Research Board, and is published by permission of the Department of Scientific and Industrial Research. The electrical measurements at the National Physical Laboratory were carried out by Mr. A. C. Gordon-Smith.

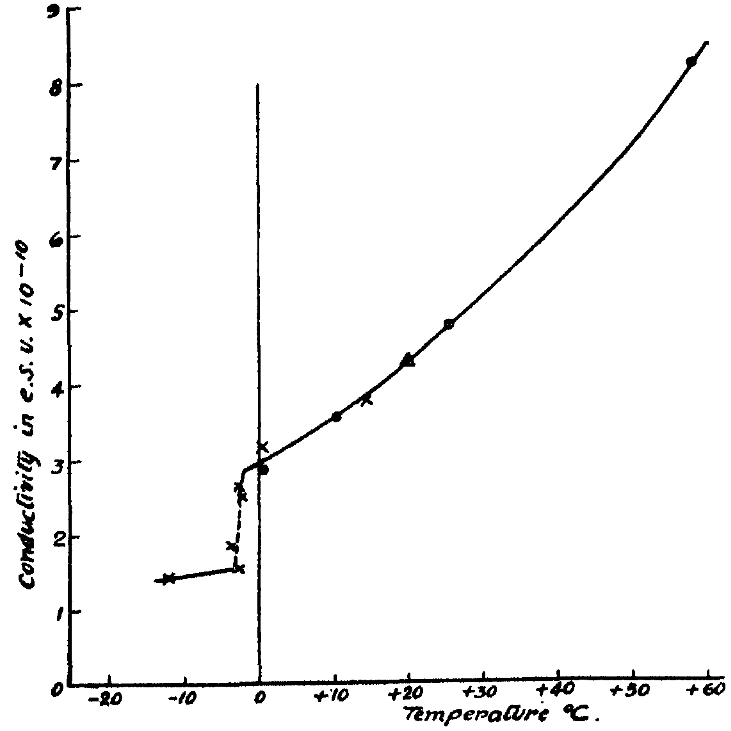

FIG. 2.—Conductivity of sea-water at various temperatures at a frequency of 1200 kilocycles per second. ⊙ First experiment, temperature 0° to 60° C.; × second experiment, temperature —12° to 15° C.; △ mean value with different lengths of condenser.

Summary.

This paper describes a laboratory investigation of the electrical properties of sea-water under alternating current conditions, with particular reference to radio frequencies. A summary of previous work carried out at various

frequencies up to 1100 kilocycles per second is given, and the experiments described afford a confirmation of the more recent results of this work together with an extension of the range of frequencies to 10,000 kilocycles per second. It is concluded that the specific conductivity of sea-water obtained from the English Channel increases from $3 \cdot 9 \times 10^{10}$ e.s.u. at a frequency of 500 cycles per second to $5 \cdot 4 \times 10^{10}$ e.s.u. at a frequency of 10,000 kilocycles per second and at a temperature of 20° C. (The corresponding resistivity values are 23 and 16·5 ohm-cm. respectively.) Evidence is given in the paper for concluding that in determining the current flowing in the sea-water within the above frequency range, the part played by the dielectric constant is negligible in comparison with the effect of the conductivity. The actual value of the dielectric constant is probably about 80 as for distilled water, the very high apparent values obtained at audio- and at low radio-frequencies being attributed to the effect of polarization films formed at the contact between the electrolyte and the electrodes.

Measurements of the conductivity carried out at different temperatures indicate that between 0° C. and 40° C. the mean temperature coefficient is about $+ 2 \cdot 7\%$ per degree C. A sudden decrease in the conductivity was observed to occur at a temperature of about $- 2°$ C., and below this transition point the temperature coefficient has a much smaller value.

The Determination of the Valency Angles of the Oxygen and Sulphur Atoms and the Methylene and Sulphoxy Groups, from Electric Dipole Moments.

By G. C. HAMPSON, R. H. FARMER, and L. E. SUTTON.

(Communicated by N. V. Sidgwick, F.R.S.—Received August 1, 1933.)

A review of the methods available for the determination of the angles between covalencies by the measurement of electric dipole moments, and the probable sources of error in them, has been given in a recent publication.*

We had made preliminary measurements on diphenyl ether and some derivatives in 1931 and 1932, when results for these substances were published by Bergmann and Tschudnowsky† and by Smyth and Walls.‡

Owing to the discrepancies in the calculated angle for the oxygen valencies reported by these authors, we decided to withhold these early results until sufficient independent data for a more complete analysis had been obtained. Accordingly the moments of diphenyl ether, the *p*-monobromo, *pp'*-dibromo, *pp'*-dimethyl, *p*-mono-nitro and *pp'*-dinitro derivatives, together with *p*-bromotoluene, were measured in benzene at 25° C., that of *p*-mono-nitro-diphenyl ether also being measured in carbon tetrachloride at 25° C.

As a check upon the method, the angle of the methylene group was calculated from the moments of diphenylmethane and the *pp'*-dibromo derivative which were also measured in benzene. It was later decided to reinvestigate the sulphur angles in the sulphides and sulphoxides, for which purpose the moments of diphenyl sulphide, diphenyl sulphoxide and their *p*-mono-chloro, *pp'*-dichloro, and *pp'*-dimethyl derivatives have been determined, again in benzene solution at 25° C.

EXPERIMENTAL.

Measurement of Electric Dipole Moments.

For determining dielectric constants the heterodyne apparatus described previously§ was used. It was slightly modified in order to eliminate errors from lead inductance so far as possible, although these were calculated to be very small since the frequency used was fairly low (450 k.c.). In any case, since they decrease as the dilution of the solution increases, they should not affect the extrapolation to infinite dilution. The step condenser F was replaced by one having quartz insulation, and the switch S was improved. In order to avoid the cumulative errors to which the dilution cell was liable, condensers for measuring single solutions were constructed. These alterations will be described in a future communication.

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* Hampson and Sutton, 'Proc. Roy. Soc.,' A, vol. 140, p. 562 (1933).

† 'Z. phys. Chem.,' B, vol. 17, p. 107 (1932).

‡ 'J. Amer. Chem. Soc.,' vol. 54, p. 3230 (1932).

§ Sutton, 'Proc. Roy. Soc.,' A, vol. 133, p. 668 (1931).

Since polarizations of solute are calculated from the difference (which is usually small) between the polarizations of solution and solvent, accuracy depends upon the exactitude with which differences, rather than absolute magnitudes, are measured. Consequently errors were eliminated so far as possible by taking as density of the solvent, and the standard scale reading difference in condensers E and F for the air-solvent change in D, those values which were got by extrapolating the d_S/f_2 and $\delta N/f_2$ curves to infinite dilution.

The probable limits of experimental error in P_2, ${}_EP_2$, and ${}_{A+O}P_2 = P_2 - {}_EP_2$ and μ are indicated in the following tables: they were computed graphically. The values for the densities used in these calculations were read off from the mean d_S/f_2 line, though the individual experimental points were seldom off this by more than one part in ten thousand.

Preparation and Purification of Materials.

Benzene.—A.R. benzene, thiophene free, was purified by three fractional freezings, and was dried first by calcium chloride, and then by being refluxed over phosphorus pentoxide in a slow stream of dry air. Finally it was distilled off into a reservoir, protected by the dry air stream, from which it could be pumped into a small receiver as required.

Carbon Tetrachloride.—Albright and Wilson's liquid for medicinal purposes was distilled from P_2O_5 and used without further purification.

Diphenyl Methane.—Diphenyl methane supplied by Hopkin and Williams was recrystallized twice from alcohol using a freezing mixture of ice and salt. M.P. 24·5–25·0° C. (corr.).*

pp′-*Dibromodiphenyl Methane.*—This was prepared by direct bromination of diphenyl methane,† the *o-p* and *o-o′* isomers being removed by washing with cold low-boiling ligroin and the *pp′*-product finally recrystallized three times from low-boiling ligroin with centrifuging. M.P. 62·6–63·0° C. (corr.).‡

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[*] 26–27° C., Zincke, 'Liebigs. Ann.,' vol. 159, p. 367 (1871); 22·75° C., Reissert, 'Ber. deuts. chem. Ges.,' vol. 23, p. 2242 (1890).

[†] Goldthwaite, 'Amer. Chem. J.,' vol. 30, p. 448 (1903).

[‡] 64·0° C., Goldthwaite, *loc. cit.*

Diphenyl Ether.—A specimen supplied by Hopkin and Williams was recrystallized twice from alcohol and centrifuged. M.P. 26·6–27·0° C. (corr.).[*]

p-*Monobromo- and* pp′-*Dibromo-diphenyl Ether.*—These were prepared by direct bromination.[†] Using equimolecular quantities of bromine and diphenyl ether, the monobrominated ether forms the bulk of the product, the *p*-derivative being freed from impurities by fractionating the liquid three times under reduced pressure and then four times under ordinary pressure. The fraction boiling at 299–301° C. (760 mm.) was finally recrystallized from alcohol using a freezing mixture. M.P. 18·2–18·8° C. (corr.).

Using twice the above quantity of bromine the *pp*′-dibromo derivative is formed almost exclusively, and careful fractionation under reduced pressure is not necessary. The bulk of the product boiled at 238°–245° C. (760 mm.) and was purified by repeated recrystallization, with centrifuging, from alcohol. M.P. 59·3–60·3° C. (corr.).[‡]

Di-p-*tolyl Ether.*—This was prepared by condensing *p*-bromtoluene with potassium *p*-cresylate according to the method of Reilly, Drumm, and Barrett.[§] After three crystallizations from alcohol, a product melting at 48·0–48·6° C. (corr.) was obtained.[||]

p-*Mononitrodiphenyl Ether and* pp-*dinitrodiphenyl Ether.*—These were prepared by condensation reactions similar to the above.[¶]

For the mononitro derivative 15·5 gm. of potassium were dissolved in 137 gm. of pure phenol (from recrystallized phenol hydrate) at 150° C. and 26 gm. recrystallized *p*-bromnitrobenzene added and the mixture heated for 14 hours at 150° C. When cold, the mixture was treated with caustic soda solution, extracted with ether, and the ethereal solution evaporated. The residue, after blowing in steam to remove unchanged bromnitrobenzene, was again extracted with ether and the dark oily product remaining after removal of the ether was recrystallized four times from methyl alcohol with centrifuging, the colouring matter being removed by refluxing the solution with animal charcoal. In this way, white crystals melting at 59·0–59·3° C. (corr.)* were obtained.

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[*] 26·9–27·0° C., Cook, 'J. Amer. Chem. Soc.,' vol. 26, p. 303 (1904).

[†] Mailhe and Murat, 'C. R. Acad. Sci. Paris,' vol. 154, p. 601 (1912); C. M. Suter, 'J. Amer. Chem. Soc.,' vol. 51, p. 2581 (1929).

[‡] 58·8–58·9° C. Smyth and Walls, *loc. cit.*

[§] 'J. Chem. Soc.,' p. 67 (1927).

[||] 50° C., *loc. cit.*

[¶] Haeussermann and Teichmann, 'Ber. deuts. chem. Ges.,' vol. 29, p. 1446 (1896); Bergmann and Tschudnowsky, *loc. cit.*

For the dinitro derivative, the method was to add carefully finely pulverized potassium *p*-nitro phenate (prepared by boiling a solution of the estimated weight of potassium carbonate with *p*-nitrophenol, cooling and crystallizing and dehydrating the crystals *in vacuo* at 130° C.), in small amounts at a time, to about four times the quantity of *p*-chlornitrobenzene at 225°–235° C. so that this temperature is maintained during the addition, which should take several hours. When cold, water was added to dissolve the potassium chloride and unchanged potassium nitrophenate, and the excess chlornitrobenzene removed by blowing in steam. The remaining brown mass was recrystallized and centrifuged from benzene six times, using a little animal charcoal each time to remove the colouring matter. Very pale yellow crystals. M.P. 144·0–144·3° C. (corr.)†

p-*Bromtoluene.*—This was prepared from *p*-toluidine by diazotization.‡ M.P. 26·0° C. (corr.).

Diphenyl Sulphide.—This was made according to the method of Mauther,§ by the action of iodobenzene on potassium thiophenolate.‖ Potassium thiophenolate was found to give a better yield than the sodium salt. The product was distilled at 285–295° C. at 762 mm., and then distilled three times under reduced pressure, collecting the middle fraction each time. A colourless oil. B.P. 152–154° C. at 14 mm.¶

p-*Chlordiphenyl Sulphide.*—This was prepared as above, using *p*-chloriodobenzene instead of iodobenzene.** The product was purified by recrystallization first from alcohol and then from ligroin (40–60°) with the aid of a freezing mixture at — 20° C. Colourless crystals. M.P. 20·6–20·8° C. (corr.).

pp′-*Dichlordiphenyl Sulphide.*—This was made by reduction of the dichlorsulphoxide by boiling with zinc dust and acetic acid, following the directions given by Gazdar and Smiles†† for the reduction of di-*p*-cresol sulphoxide.

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* 58° C., Bergmann and Tschudnowsky, *loc. cit.*; 61° C., Haeussermann and Teichmann, *loc. cit.*

† 142·5–143·0° C., Haeussermann and Teichmann, *loc. cit.*; 144·4–144·7° C., Smyth and Walls, *loc. cit.*

‡ Sandmeyer, 'Ber. deuts. chem. Ges.,' vol. 17, p. 2651 (1884).

§ 'Ber. deuts. chem. Ges.,' vol. 39, p. 3594 (1906).

‖ Burgeois, 'Ber. deuts. chem. Ges.,' vol. 28, p. 2319 (1895).

¶ 154° C. at 13 mm., Bergmann, Engel, and Sandor, 'Z. phys. Chem.,' B, vol. 10, p. 397 (1930).

** Bergmann and Tschudnowsky, *loc. cit.*

†† 'J. Chem. Soc.,' vol. 97, p. 2250 (1910).

Recrystallization from ligroin (80°–100°) gave a 75% yield of a product melting at 94·2–94·5° C. (corr.).

Di-p-*tolyl Sulphide.*—Reduction of the sulphoxide by Clemensen's method was used. A mixture of 18 gm. of di-*p*-tolyl sulphoxide dissolved in 200 c.c. of alcohol and 70 gm. of zinc wool which had been amalgamated for 3 hours in a 5% solution of mercuric chloride, was refluxed on a water bath for 3 hours. The alcohol was then distilled off, the residue extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate. After removal of the ether, the product solidified on cooling and purified by recrystallizing four times from alcohol. M.P. 56·6–56·9° C. (corr.).*

Diphenyl Sulphoxide.—The method of Colby and McLoughlin† was used, namely, treating benzene with thionyl chloride in the presence of aluminium chloride. M.P. 70·5–70·8° C. (corr.).‡

p-*Chlordiphenyl Sulphoxide.*—This was prepared by oxidizing the corresponding sulphide with hydrogen peroxide§ and recrystallizing the product three times from ligroin (40–60°). M.P. 42·8–43·2° C. (corr.).‖

pp′-*Dichlordiphenyl Sulphoxide.*—The method of preparation was similar to that used for making diphenyl sulphoxide. 40 gm. of dry redistilled chlorbenzene were mixed with 26 gm. of thionyl chloride and aluminium chloride added slowly. Hydrogen chloride ceased to be evolved when about 39 gm. of aluminium chloride had been added. The mixture was left to stand for 2 hours, as it was found that on warming it darkened considerably. The liquid was then poured into water containing a large quantity of ice, when the product was obtained as a nearly white solid which crystallized well from alcohol. After three crystallizations, the melting point was constant at 143·4–143·7° C. (corr.)¶ and was unaltered by a further crystallization from benzene. Yield 17 gm. pure product.

Di-p-*tolyl Sulphoxide.***—The method of preparation was similar to that just described. Repeated recrystallization from ligroin (100–120°) with animal charcoal gave a product melting at 94·9–95·4° C. (corr.).††

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* 56–57° C., Otto, 'Ber. deuts. chem. Ges.,' vol. 12, p. 1176 (1879); 57·3° C. (corr.), Bourgeois, *ibid.*, vol. 28, p. 2325 (1895).

† 'Ber. deuts. chem. Ges.,' vol. 20, p. 197 (1887).

‡ Colby and McLoughlin give M.P. 70·5° C.

§ Bergmann and Tschudnowsky, 'Ber. deuts. chem. Ges.,' vol. 65, p. 460 (1932).

‖ 45–46° C., Bergmann and Tschudnowsky, *loc. cit.*

¶ 143–145° C., Bergmann and Tschudnowsky, 'Ber. deuts. chem. Ges.,' vol. 65, p. 460 (1932).

** Parker, 'Ber. deuts. chem. Ges.,' vol. 23, p. 1845 (1890).

†† 92° C., Parker, *loc. cit.*

Dipole Moments.—The data for the determination of dipole moments are given in the following tables, where

f_2 = molecular fraction of the solute.
e = dielectric constant of the solution, at 25° C.
n = refractive index of the solution at 25° C.
d_s = density of the solution at 25° C.
P_2 = total polarization of the solute.
$_eP_2$ = electron polarization of the solute.

All dipole moments are expressed in terms of the Debye unit, 10^{-18} e.s.u.

Diphenyl Methane.

f_2.	d_s.	e.	n^2.	P_2.	$_eP_2$.
0·037758	0·8831	2·29186	2·27381	57·19	55·68
0·027937	0·8812	—	2·26994	—	55·90
0·022363	0·8795	2·28393	—	56·96	—
0·019953	0·8787	2·28412	2·26638	57·75	55·96
0·010053	0·87625	2·27768	2·26185	57·15	55·88

pp′-Dibromdiphenyl Methane.

0·01861	0·9040	2·37817	2·27386	143·62	73·28
0·017606	0·9023	2·37316	—	144·37	—
0·013628	0·8959	2·35116	2·26949	145·29	73·58
0·010555	0·8909	2·33194	2·26650	143·46	73·38
0·008634	0·8877	2·32179	—	144·97	—
0·006685	0·8846	2·31147	2·26308	146·85	73·49

Diphenyl Ether.

0·028768	0·8843	2·33726	2·27025	79·79	52·88
0·015594	0·8795	2·30856	2·26418	80·55	52·65
0·009210	0·8771	2·29375	2·26132	80·78	52·87
0·007442	0·8764	2·28944	2·26035	80·71	52·62

p-Monobrom-diphenyl Ether.

0·028634	0·9044	2·39112	2·27617	112·12	60·89
0·024084	0·8996	2·37102	2·27386	111·42	61·33
0·017672	0·8927	2·34604	2·26884	112·66	60·98
0·007655	0·8821	2·30468	2·26242	112·92	60·81

pp′-Dibrom-diphenyl Ether.

f_2.	d_2.	ϵ.	n^2.	P_2.	$_EP_2$.
0·028374	0·9240	2·30883	2·28294	75·34	69·59
0·020762	0·9105	2·29966	2·27626	76·09	70·42
0·011329	0·8939	2·28727	2·26732	75·92	70·03

Di-*p*-tolyl Ether.

0·020204	0·8803	2·33746	2·26563	104·95	62·95
0·015576	0·8788	2·32284	2·26339	104·99	62·66
0·009029	0·8768	2·30134	2·26103	103·91	62·71

p-Mononitro-diphenyl Ether (in benzene).

0·014131	0·88414	2·64878	2·26799	414·78	60·92
0·0093052	0·88066	2·51990	2·26364	422·98	61·31
0·0068482	0·87893	2·45433	2·26225	427·12	61·94
0·0045193	0·87724	2·39278	2 26103	433·4	63·79

p-Mononitro-diphenyl Ether (in carbon tetrachloride).

0·0104435	1·57847	2·48305	2·14226	430·24	62·00
0·0075587	1·58005	2·41172	—	434·62	—
0·0049215	1·58152	2·34699	2·13752	439·36	62·72
0·0037898	1·58216	2·31998	—	444·42	—

pp′-Dinitro-diphenyl Ether.

0·013268	0·88853	2·41424	2·27093	208·7	70·1
0·010299	0·88526	2·38215	2·26800	209·05	70·5
0·0073148	0·88206	2·35098	2·26508	210·38	70·9
0·0056315	0·88022	2·33263	2·26293	209·87	70·2

p-Bromotoluene.

0·017174	0·8860	2·36092	2·25990	116·56	38·26
0·012010	0·8822	2·34140	2·25886	117·52	38·10
0·008119	0·8796	2·31971	2·25826	117·2	37·91

Diphenyl Sulphide.

0·025850	0·88571	2·37504	2·27711	107·3	60·49
0·017783	0·88205	2·34307	2·27153	107·5	61·14
0·015026	0·88079	2·33277	2·26911	108·0	60·89
0·007175	0·87718	2·30117	2·26303	107·9	61·45

p-Monochlor-diphenyl Sulphide.

f_2.	d_2.	ϵ.	n^2.	P_2.	${}_{E}P_2$.
0·022903	0·89020	2·36807	2·27798	114·2	65·89
0·017918	0·88674	2·34681	2·27328	113·9	66·26
0·011767	0·88238	2·32223	2·26789	114·9	66·31
0·005625	0·87798	2·29599	2·26220	114·0	66·21
0·003961	0·87676	2·28936	2·26064	115·3	66·26

pp′-Dichlor-diphenyl Sulphide.

0·018505	0·89162	2·29970	2·27553	79·22	71·93
0·013050	0·88650	2·29162	2·27012	79·06	71·96
0·008548	0·88222	2·28519	2·26574	79·31	72·25
0·004011	0·87794	2·27858	2·26124	79·23	72·37

Di-*p*-tolyl Sulphide.

0·019551	0·88229	2·38931	2·27269	146·98	71·19
0·012552	0·87929	2·34790	2·26735	147·61	71·54
0·008039	0·87737	2·32134	2·26359	148·60	71·40
0·0042626	0·87578	2·29827	2·26056	147·87	71·34

Diphenyl Sulphoxide.

0·018868	0·88620	2·71592	2·27258	366·2	60·90
0·013774	0·88293	2·59538	2·26839	372·3	60·90
0·009485	0·88015	2·49509	2·26509	378·7	61·30
0·005391	0·87744	2·39903	2·26178	384·9	61·95

p-Monochlor-diphenyl Sulphoxide.

0·012212	0·88495	2·49830	2·26798	313·6	65·82
0·009753	0·88272	2·45207	2·26583	314·7	66·02
0·007703	0·88082	2·41269	2·26405	313·7	66·39
0·007071	0·88026	2·40069	2·26368	313·3	66·83
0·004603	0·87812	2·35653	2·26124	316·6	66·09

pp′-Dichlor-diphenyl Sulphoxide.

0·008622	0·88384	2·36165	2·26586	207·1	71·91
0·007921	0·88304	2·35461	2·26506	207·6	71·75
0·006917	0·88193	2·34438	2·26410	207·9	71·72
0·005896	0·88075	2·33393	2·26311	208·5	71·91
0·004902	0·87961	2·32332	2·26229	208·0	72·52
0·004604	0·87923	2·31995	2·26186	207·4	72·39

Di-*p*-tolyl Sulphoxide.

f_2.	d_2.	ϵ.	n^2.	P_2.	$_EP_2$.
0·021742	0·88738	2·88950	2·27480	432·6	70·86
0·015773	0·88357	2·71884	2·26959	442·6	70·79
0·010773	0·88060	2·57672	2·26597	451·4	71·32
0·007495	0·87855	2·48437	2·26325	458·0	71·06
0·007251	0·87838	2·47787	2·26314	459·2	71·32
0·004120	0·87644	2·38886	2·26062	464·5	71·49

Limits of Experimental Error in Polarizations at Infinite Dilution, and the Calculated Dipole Moments.

Substance.	P_2.	$_EP_2$.	$_{A+O}P_2 = P_2 - {}_EP_2$.	μ.
Ph_2CH_2	57·0– 57·3	55·9–56·0	1·0– 1·4	0·22–0·26
$(BrC_6H_4)_2CH_2$	145·0–146·8	73·4–73·8	71·2– 73·4	1·85–1·88
Ph_2O	80·9– 81·2	52·6–52·9	28·0– 28·6	1·16–1·17
p-BrC_6H_4O . Ph	113·0–113·6	60·8–61·2	51·8– 52·8	1·58–1·60
(*p*-$BrC_6H_4)_2$. O	75·7– 76·2	69·6–70·4	5·3– 6·6	0·51–0·56
(*p*-$CH_3C_6H_4)_2$. O	104·0–105·0	62·5–62·8	41·2– 42·5	1·41–1·43
p-$NO_2C_6H_4O$. Ph (in benzene)	440 –443	61·5–63·0	377·0–381·5	4·26–4·29
p-$NO_2C_6H_4O$. Ph (in CCl_4)	447 –452	62·0–63·0	384 –390	4·30–4·34
(*p*-$NO_2C_6H_4)_2$. O	210·5–213·0	70·3–71·0	139·5–142·7	2·60–2·62
$BrC_6H_4CH_3$	117·2–118·2	37·9–38·3	78·9–80·3	1·95–1·97
Ph_2S	107·8–108·5	60·8–61·8	46·0– 47·8	1·49–1·51
p-ClC_6H_4S . Ph	114·0–115·5	66·2–66·5	47·5– 49·3	1·51–1·54
(*p*-$ClC_6H_4)_2$. S	79·1– 79·3	72·0–72·4	6·7– 7·3	0·57–0·59
(*p*-$CH_3C_6H_4)_2$. S	148·2–149·2	71·2–71·6	76·6– 78·0	1·92–1·94
Ph_2SO	391·5–393·0	61·0–61·5	330 –332	3·99–4·00
p-ClC_6H_4PhSO	314·5–318·5	66·0–67·0	247·5–251·5	3·46–3·48
(*p*-$ClC_6H_4)_2SO$	208·4–210·4	71·7–72·5	135·9–138·7	2·56–2·58
(*p*-$CH_3C_6H_4)_2SO$	471·5–473·0	71·0–71·5	400 –402	4·39–4·40

Discussion of Results.

Calculation of Angles.—The values of the angle θ, between the Ph–X valencies, where X is CH_2, O, or S, were calculated by the methods described previously.* The substances and the moments taken to give μ_0, μ_S, and μ_T are stated for each calculation.

The angles calculated from the mono-substituted products are unambiguous but this is not true of those from the di-substituted products. As mentioned in the footnote on p. 568 of the previous paper, it is necessary to know the relative senses of μ_0 and μ_T as well as their magnitudes. For the dibromodiphenyl methane there is little doubt that μ_0 is similar in sense to the moment of toluene, and therefore μ_0 and μ_T are in the same sense. Ditolyl ether and ditolyl sulphide are similar. Again in the dinitro derivative, μ_S, which is the moment of $PhNO_2$, is certainly much larger than μ_{Ph-O}, and hence μ_T is opposite in sense to μ_0. There is, however, no means of knowing *a priori* whether μ_T is in the same or the opposite sense to μ_0 in the dibromo ether or the dichloro sulphide; in these, μ_0 and μ_S are in opposite senses, and the sense of μ_T depends upon whether $\frac{\mu_0}{2\cos\theta/2}$ is numerically greater or less than μ_S (see fig. 1). Values calculated on either basis are given in the tables, and the direction assumed for the resultant is indicated as $\overset{+\!\longrightarrow}{\text{HalPhX}}$ or $\overset{\longleftarrow\!+}{\text{HalPhX}}$ respectively.

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* Hampson and Sutton, *loc. cit.*, pp. 565–568.

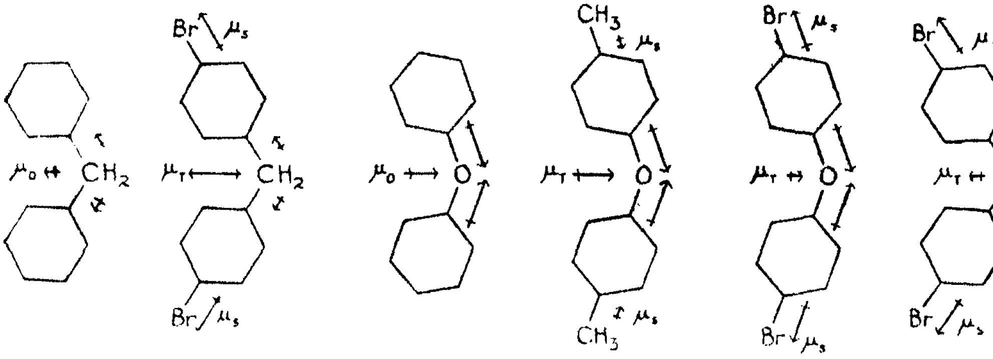

FIG. 1.

The Carbon Angle in Diphenyl Methane.

Solution No.	μ_0.		μ_S.		μ_T.		θ.
1	Ph_2CH_2	0·24	PhBr	1·52	$(BrC_6H_4)_2CH_2$	1·87	117°

For the ethers the angle must, from the unambiguous solutions 1 and 3, be approximately 140°, wherefore the larger values given by the dibromo compounds in solutions 2 and 4 are taken as correct. This means that $\mu_{Ph-O} = 1{\cdot}74 > \mu_{Ph-Br} = 1{\cdot}52$, taking the angle to be 142°. For the thioethers, the angle must be approximately 118° from solutions 1 and 3,* and

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* The solution obtained from diphenyl sulphide and the monochloro derivative is undoubtedly the most accurate, for all the moments concerned are large, and the solution is unambiguous.

The Oxygen Angle in Diphenyl Ether.

Solution No.	μ_0.	μ_S.	μ_T.	θ.
1*a*	$\mathrm{Ph_2O}$ 1·16–1·17	PhBr 1·52	$\mathrm{BrC_6H_4OPh}$ 1·58–1·60	141–144
1*b*			For $\mathrm{P_A}$=5 c.c. μ=1·52	135
2*a*	$\mathrm{Ph_2O}$ 1·16–1·17	PhBr 1·52	$\mathrm{(BrC_6H_4)_2O}$ 0·52	+→ 155 ←+ 112·5
2*b*			For $\mathrm{P_A}$=5 c.c. μ=0·17	+→ 141 ←+ 128
3	$\mathrm{Ph_2O}$ 1·16–1·17	$\mathrm{PhCH_3}$ 0·40*	$\mathrm{(CH_3C_6H_4)_2O}$ 1·41–1·43	140·5–145
4*a*	$\mathrm{(BrC_6H_4)_2O}$ 0·52	$\mathrm{CH_3C_6H_4Br}$ 1·97	$\mathrm{(CH_3C_6H_4)_2O}$ 1·41–1·43	+→ 153 ←+ 121
4*b*	For $\mathrm{P_A}$=5 c.c. μ=0·17			+→ 143 ←+ 132
5	$\mathrm{Ph_2O}$ 1·16–1·17	$\mathrm{PhNO_2}$ 3·93	$\mathrm{NO_2C_6H_4OPh}$ 4·26–4·33	Unreal $>$ 180
6	$\mathrm{Ph_2O}$ 1·16–1·17	$\mathrm{PhNO_2}$ 3·93	$\mathrm{(NO_2C_6H_4)_2O}$ 2·60–2·62	122–123

The Sulphur Angle in Diphenyl Sulphide.

1	$\mathrm{Ph_2S}$ 1·49–1·51	PhCl 1·56	$\mathrm{ClC_6H_4SPh}$ 1·51–1·54	118–121
2*a*	$\mathrm{Ph_2S}$ 1·49–1·51	PhCl 1·56	$\mathrm{(ClC_6H_4)_2S}$ 0·58	+→ 145·5 ←+ 96·5
2*b*			For $\mathrm{P_A}$=5 c.c. μ=0·31	+→ 135 ←+ 109
3	$\mathrm{Ph_2S}$ 1·49–1·51	$\mathrm{PhCH_3}$ 0·40*	$\mathrm{(CH_3C_6H_4)_2S}$ 1·92–1·94	112–118·5

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* In view of the recent work of McAlpine and Smyth (' J. Amer. Chem. Soc.,' vol. 55, p. 453 (1933)) and of Fuchs and Donle (' Z. phys. Chem.,' B, vol. 22, p. 1 (1933)) on the moment of toluene, the value now taken for this is 0·40.

therefore the smaller values in solution 2 are considered correct. On this basis, for $\theta = 118°$, $\mu_{Ph-S} = 1 \cdot 46 < \mu_{Ph-Cl} = 1 \cdot 56$.

Errors arising out of neglected Atom Polarization and Interaction between Groups.—From the discussion of possible errors given on pp. 572–577 of the previous paper (Hampson and Sutton, *loc. cit.*), it will be evident that, in any case, the angles calculated from the dibromo ether and dichloro sulphide are the least reliable; not only are the atom polarizations likely to be appreciable in these compounds, which contain the largest number of fairly big component dipoles, but also the proportional error in the resultant moment due to neglect of this quantity is larger the smaller the moment. In order to show how the results are affected by this, they are recalculated after an arbitrary allowance of 5 c.c. has been made for P_A; this brings them more into line with the other values. A similar allowance was made in order to ascertain the possible error with the monobromo ether, but the angle so calculated is a minimum possible value, for P_A is unlikely to be as much for this as for the dibromo derivative (where it cannot possibly be more than 6 c.c.) and no allowance for P_A^A in μ_0 or μ_S has been made; if this be done, the angle calculated is greater.

So far as errors due to interaction of the groups in the para positions to the bridging atom or group are concerned,* it will be observed that, since in dibromodiphenyl methane, ditolyl ether and ditolyl sulphide, ρ, the angle between μ_0 and either substituent moment μ_S, is $< 90°$, the di-substituted compound will give a more accurate value of ρ, and therefore θ, than the mono-substituted one. The condition for $\delta_1\rho$, the error in the angle calculated from the mono-substituted compound to be numerically less than $\delta_2\rho$, that from the di-substituted one, is that

$$\frac{1-n}{n} > \frac{\mu_S}{\mu_0 \cos \rho} > -\frac{n+1}{n}$$

and not the one given in the previous paper (p. 576).

Since $\mu_S/\mu_0 \cos \rho$ for the bromo ethers and chloro sulphides is $-3 \cdot 93$ and $-2 \cdot 1$ respectively, it lies for both types below these limits, which are 0 to -2 if n is unity, and $-\frac{1}{2}$ to $-1\frac{1}{2}$ if n is 2. Thus $\delta_1\rho$ is numerically $> \delta_2\rho$ and, moreover, since $n\left(1 + \frac{\mu_S}{\mu_0 \cos \rho}\right)$ is negative, these errors are opposite in sign, which means that the true value of ρ, and therefore θ, must lie *between* the values obtained from the mono- and di-substituted compounds.† In other words, so far as this source of error is concerned, the values of the angle got by the two methods represent upper and lower limits.

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* Hampson and Sutton, *loc. cit.*, p. 572.

† In general, the condition that this should be so is that $1 + \frac{\mu_S}{\mu_0 \cos \rho} < 0$, *i.e.*, that $\cos \rho > -\frac{\mu_S}{\mu_0}$, hence if $\mu_S > \mu_0$ this condition is necessarily satisfied.

The nitro ethers are the only ones giving really anomalous results. The physical significance of this is that the interaction of the groups through the rings, and the additional moment $\delta\mu_S$ thereby created, are large. Consequently, if $\delta\mu_S$ is in the same sense as μ_S, the moment caused by substitution is really larger than the moment of nitrobenzene, and hence

$$\cos\rho = \cos\left(180^\circ - \frac{\theta}{2}\right),$$

as calculated for the mononitro compound is positive, while for the dinitro compound it is numerically too large. Equations including interaction moments can be constructed for both compounds, and if it be assumed that $\delta_1\mu_S = \delta_2\mu_S$, they may be combined to give a value for θ independent of the interaction moment, as follows.

Suppose there is an interaction moment $\delta\mu_S$ created along the axis of the benzene ring in the same direction as the moment of the nitro group, then the moment μ_T of the mono-substituted derivative is given by

$$\mu_T^2 = \left(\frac{\mu_O}{2\cos\theta/2}\right)^2 + \left(\mu_S - \frac{\mu_O}{2\cos\theta/2} + \delta\mu_S\right)^2 - 2\cos\theta\left(\frac{\mu_O}{2\cos\theta/2}\right)\left(\mu_S - \frac{\mu_O}{2\cos\theta/2} + \delta\mu_S\right).$$

If the same interaction moment $\delta\mu_S$ is created along both rings in the di-substituted derivative, the moment μ'_T of this latter compound is given by

$$\mu'_T = 2\cos\theta/2\left(\mu_S - \frac{\mu_O}{2\cos\theta/2} + \delta\mu_S\right).$$

Solving these two equations for θ and $\delta\mu_S$ we get

$$\theta = 2\cos^{-1}\sqrt{\frac{\mu_O^2 + \mu'^2_T + 2\mu_O\mu'_T}{4\mu_T^2 + 4\mu_O\mu'_T}} = 132^\circ,$$

and

$$\delta\mu_S = \frac{\mu'_T + \mu_O}{2\cos\theta} - \mu_S = 0{\cdot}7.$$

This assumption is only approximate, but the result shows that when some allowance for interaction is made, a more normal result is obtained. Such interaction appears to be negligible in *pp'*-dinitrodiphenyl methane, for the angle obtained from the moment of this and diphenyl methane* agrees well with that from the latter and the dibromo derivative; since carbon ($M_D = 2 \cdot 42$) is more polarizable than ethereal oxygen ($M_D = 1 \cdot 64$) this result shows that the effect in the ethers is not a simple polarization.*

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* Bergmann, Engel, and Wolff, 'Z. phys. Chem.,' B, vol. 17, p. 81 (1932).

The only other possible general error is that arising out of the effect of non-polar solvents on the dipole moments of substances measured in them. This has been discussed by Smallwood,† and by Fuchs and Donle (*loc. cit.*), but the only evidence yet published of any general effect, rather than of specific ones on certain types of molecule in certain solvents, appears to be that of Müller.‡ Lacking further data, no general discussion of this phenomenon seems warranted here, but it may be pointed out that if it should prove that the moment of a molecule may be expressed as the product of the moment observed from the temperature coefficient of the polarization of the vapour and of a constant characteristic of the solvent but independent of the solute, *i.e.*, as $k\mu_{\text{vapour}}$, then angles calculated from moments measured in the same solvent will be accurate, because k will cancel from the angle equations.

Having regard to all the possible errors at present assessable, we may conclude from the above data that the most probable value of the angle between the axes of the phenyl groups is 115° ± 5° in diphenyl methane, 142° ± 8° in diphenyl ether, and 118° ± 8° in diphenyl sulphide.

A Review of Results obtained by other Investigators.

The values obtained by previous workers show considerable variation, and it remains now to compare them with our results, and if possible explain the discrepancies.

The agreement for the angle between the phenyl groups in diphenyl methane is reasonably good. From the moments of diphenyl methane (0·3) and *pp'*-dinitrodiphenyl methane (4·29), Bergmann, Engel, and Wolff (*loc. cit.*) calculate an angle of 120°, and they get a simliar value from the moments of diphenyl methane and the *pp'*-dibrom derivative (1·79). The value from triphenyl methane and the *pp'p''*-trinitro derivative, 114°, is similarly normal. Values of 114–119° got by Smyth and Walls§ for the carbon angle in a different type of methylene compound, namely, benzyl chloride and cyanide and their *p*-substituted derivatives, also agree with our results.

The variations in the values for the oxygen and sulphur angles, however, are

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* *Vide* Hampson and Sutton, *loc. cit.*, p. 575.

† 'Z. phys. Chem.,' B, vol. 19, p. 242 (1932).

‡ Müller, 'Phys. Z.,' vol. 33, 731 (1932).

§ 'J. Amer. Chem. Soc.,' vol. 54, p. 1854 (1932).

considerable, as appears from the following tables, column 4. These discrepancies appear to be due to three causes: (1) arithmetical errors, (2) different assumptions about the sign of the moment μ_T relative to μ_0, (3) different values being taken for the moments. The effects of the first two are shown in column 5, where the angles are recalculated using the respective authors' own data, but using our assumptions (p. 156) regarding the sign of μ_T relative to μ_0.

The Oxygen Valency Angle.

μ_0.	μ_S.	μ_T.	θ reported.	θ recalculated.
			°	°
Ph_2O 1·13	PhBr 1·49	BrC_6H_4OPh 1·76	166*	166
Ph_2O 1·05	PhBr 1·50	BrC_6H_4OPh 1·57	124†	147
Ph_2O 1·05	PhBr 1·50	$(BrC_6H_4)_2O$ 0·6	113†	162
Ph_2O 1·13	$PhCH_3$ 0·40	$CH_3C_6H_4OPh$ 1·31	144*	144
Ph_2O 1·13	$PhNO_2$ 3·98	$NO_2C_6H_4OPh$ 4·2	186* (unreal)	unreal
Ph_2O 1·05	$PhNO_2$ 3·98	$(NO_2C_6H_4)_2O$ 2·8	122†	122

The Sulphur Valency Angle.

Ph_2S 1·47	PhCl 1·56	ClC_6H_4SPh 1·70	137*	137
Ph_2S 1·47	PhCl 1·56	$(ClC_6H_4)_2S$ 0·89	158*	82
Ph_2S 1·47	PhBr 1·50	$(BrC_6H_4)_2S$ 0·6	146†	93

The anomalies of the nitro ethers have already been discussed. The other anomalies in column 5 are due to different values being taken for the moments, *e.g.*, Bergmann's value of 1·76 for the moment of *p*-bromdiphenyl ether is high (*cf.* Smyth's value of 1·57 and our value of 1·59) as also is his value of 1·70 for the moment of *p*-chlordiphenyl sulphide (*cf.* our value of 1·52). It will, therefore, be seen that when inexact values are eliminated, our results and those of other authors for the same sets of compounds agree substantially, and, further, that when some allowance is made for atom polarization when the moments are small, the results from different compounds agree among themselves.

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* Bergmann and Tschudnowsky, 'Z. phys. Chem.,' B, vol. 17, p. 107 (1932); Bergmann, Engel, and Sándor, 'Z. phys. Chem.,' B, vol. 10, p. 397 (1930).

† Smyth and Walls, 'J. Amer. Chem. Soc.,' vol. 54, p. 3230 (1932).

Applications of these Results to similar Compounds.—As was shown in the previous paper,[*] it is possible to calculate the magnitude and direction of the O–CH$_3$ link in anisole, from a knowledge of the angle ϕ, between the resultant moment of anisole and the axis of the benzene ring, and of the moment of the Ph–O link. The former is about 76° (*loc. cit.*), the latter 1·74 (p. 156) and therefore the moment of the O–CH$_3$ link is 2·33, and it is at an angle of 150° to the Ph–O link. If we may further assume that the moment of the O–CH$_3$ link in anisole is the moment which this covalency has in dimethyl ether, then from the known moment (1·32) of this latter compound we may calculate the oxygen angle in this to be 147°. Another interesting application of these results is to hydroquinone dimethyl ether. If there is complete freedom of rotation of the O–CH$_3$ groups in this compound, then it is possible to calculate the oxygen angle from the measured moment μ_0 of the compound and the moment of the O–CH$_3$ link.[†]

If θ is the oxygen angle, then

$$\mu_0 = \sqrt{2}\,\mu_{\text{O}-\text{CH}_3} \cos(\theta - 90^\circ) \qquad (1)$$

$$\mu_0 = 1{\cdot}70,\ddagger \qquad \mu_{\text{O}-\text{CH}_3} = 2{\cdot}33. \qquad \text{therefore } \theta = 149^\circ.$$

Since the moments of Ph–O and CH$_3$–O may be affected, and affected to varying amounts, by the possible electrometric effect in diphenyl ether and anisole, these assumptions are only approximate, but the calculations do indicate that if, as appears likely, the oxygen angle in diphenyl ether is of the order of 140°, the oxygen angle in other ethers, both aromatic and aliphatic, also has a large value.

A similar application can be made of sulphur to diphenyl disulphide Ph . S . S . Ph, where, owing to the improbability of a cis-configuration in the molecule coinciding with a co-planar position of the benzene rings, rotation is probably only slightly impeded. The moment of this compound is 1·81[§] and $\mu_{\text{Ph}-\text{S}} = 1{\cdot}46$ (p. 158), therefore substituting in equation (1) $\theta = 119^\circ$. Here again, therefore, the value is in agreement with that got for the sulphur angle in the thioethers. The abnormally large moment of *pp'*-dinitrodiphenyl disulphide is further evidence of group interaction.

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[*] Hampson and Sutton, *loc. cit.*, p. 507.

[†] Williams, 'Z. phys. Chem.,' A, vol. 138, p. 75 (1928); Wolf and Fuchs, "Stereochemie," p. 268 (Freudenberg), Leipzig (1932).

[‡] Williams, 'Phys. Z.,' vol. 29, p. 271 (1928); Hassel and Naeshagen, 'Z. phys. Chem.,' B, vol. 8, p. 357 (1930); Weissberger and Sängewald, 'Phys. Z.,' vol. 30, p. 792 (1929).

[§] Bergmann and Tschudnowsky, 'Z. phys. Chem.,' B, vol. 17, p. 107 (1932).

The only published values available until recently of the dipole moments of phenol and its *p*-substituted compounds gave very discordant values of θ,[*] but those of Donle and Gehrckens[†] give much more concordant values. These are shown in the table below, the moments taken being those in which no allowance is made for atom polarization.

p-substituent.	Moment of *p*-substituent derivative. μ_p.	ϕ.	μ_s.
Cl	2·27	88·5°	1·56
Br	2·18	92	1·52
CH	1·64	87	0·40
NO	5·04	48·5	3·93

μ (phenol) 1·61

Neglecting the last of these, which will be discussed later, the average value of ϕ is 90°. Assuming μ_{Ph-O} to be the same in this compound as it is in diphenyl ether, 1·74, the angle θ between the oxygen valencies in phenol is calculated to be 137° and μ_{O-H} to be 2·37. This value for μ_{O-H} is at first sight surprisingly large, but it cannot be less than 1·61, the moment of phenol, and it could only be as low as this if μ_{Ph-O} was zero. Assuming now that μ_{O-H} is the same in water as in phenol, then from the known moment of water, 1·84, it follows that the oxygen valency angle in this compound is 134°.

p-nitrophenol gives an abnormal value of ϕ which is explained by the occurrence of an interaction moment about equal to that estimated in the nitro diphenyl ethers. Again Donle and Gehrckens (*loc. cit.*) give a new value of *p*-nitro-anisole, 4·78, which, unlike the earlier one of Højendahl,[‡] 4·36, gives an abnormally low value, 50°, for ϕ and indicates an interaction moment of about 0·5. This is in harmony with our conclusions in this and the previous paper.

Diphenyl Sulphoxide.—Bergmann and Tschudnowsky[§] showed, from dipole moment measurements, that in sulphoxides the three sulphur covalencies were not co-planar. A computation of the actual angles has already been made from their data,* but it was thought desirable to repeat the measurements and to extend them. The angle θ between the axes of the two benzene rings can be calculated in two ways.† Using our data for diphenyl sulphoxide and the *p*-chlor and *pp'*-dichlor derivatives, θ is found to be 111°, whilst the value got from the moments of diphenyl sulphoxide and the *pp'*-dichlor and di-*p*-tolyl derivatives is 112°. It must be admitted that this good agreement is probably fortuitous, for the nature of the formulæ used makes the calculated angles very susceptible to small errors in the individual moments. If μ_T is changed by 0·02 the resulting angle calculated from equation (8) is changed by 3·5°. Owing to the magnitude of all the moments concerned, the experimental error is probably small, but even so, the angle calculated by this method cannot be relied on within closer limits than ± 8°. When calculated by the second method, the angle is very sensitive to small changes in μ_S' the moment of toluene, so that again the possible error is large, say, ± 10°.

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[*] Hampson and Sutton, *loc. cit.*, p. 573.

[†] 'Z. phys. Chem.,' B, vol. 18, p. 306 (1932).

[‡] "Studies in Dipole Moment," 'Dissertation.' Copenhagen (1929); *cf.* Hampson and Sutton, *loc. cit.*, p. 575.

[§] 'Ber. deuts. chem. Ges.,' vol. 65, p. 457 (1932).

For the purpose of calculating the other angles in the molecule by means of equations (9) and (10) (p. 569) θ will be taken as 112°. Assuming that the moment of the Ph–S bond in diphenyl sulphoxide is the same as it is in diphenyl sulphide, *i.e.*, 1·46 (p. 158), it is found that the angle τ between the $S \rightarrow O$ link and each of the Ph–S links is 115°, and that the moment of the $S \rightarrow O$ link is 2·63. Since the moment of a co-ordinate link can be as much as 7 to 8, this value shows that in this particular one there must be considerable asymmetry of sharing, which reduces the moment. That it is approximately correct follows, however, from the fact that if the moment of diphenyl sulphone be calculated from the above values for the moments of the Ph–S and $S \rightarrow O$ bonds, a value of 4·73 is obtained, in satisfactory agreement with that of 5·05 found by de Vries and Rodebush.‡

The Significance of the Results.

The results obtained by other authors and by ourselves from dipole moments may be summarized as follows. The angle between the valencies of carbon is usually between 109·5° and 120°, but may sometimes be greater§; variations with the nature of the groups attached occur in such a way as to support the general ideas of the Thorpe-Ingold theory of the distortion of valency angles.‖

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* Hampson and Sutton, *loc. cit.*, p. 578.

† *Loc. cit.*, pp. 569 and 570.

‡ 'J. Amer. Chem. Soc.,' vol. 53, p. 2888 (1931).

§ Hampson and Sutton, *loc. cit.*, p. 564.

‖ Ingold, 'J. Chem. Soc.,' vol. 119, p. 305 (1921).

If two of the bonds form a double bond, the angle between the other two is about 120°–130°,* the angle from the Van't Hoff theory being 125·25°.

The angle between the oxygen valencies in the ethers is about 140°; it appears to be slightly less in water, but the angle found is still considerably bigger than that (90°) indicated by the infra-red absorption spectra for this substance, or for chlorine monoxide.† The angle in the ethers is also larger than that found from the collision area method.‡

The angle between the sulphur valencies in the thioethers is about 118°. It may be less in hydrogen sulphide; Dadieu and Kohlrausch§ concluded that it was 90° from the Raman spectrum. In the sulphoxides the angles between all the pairs of valencies are approximately 115°, in the sulphones 110°.||

The valency angles of the other elements of Group VI have not yet been determined, nor have those of any in Group V, but the finite moments of the hydrides,¶ aryls** and halides†† of these elements show that the angle is $< 180°$ in Group VI and $< 120°$ in Group V. The non-polarity of boron trichloride indicates, however, that in this the co-valencies are at 120° to one another.

The significance of these results is as yet uncertain. The large angle for oxygen may be due—

(*a*) to the natural angle being greater than that of carbon or sulphur;
(*b*) to the forces between the valencies or the groups attached to them being different;
(*c*) to the force constants of valency bending being different;
(*d*) to combinations of these factors.

According to Pauling's hypothesis‡‡ the first explanation is incorrect, the natural angle for both oxygen and sulphur being about 90°. His view would be strongly supported if it were proved beyond doubt that the angle in water or chlorine monoxide was 90–110°.

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* Bergmann, Engel, and Meyer, 'Ber. deuts. chem. Ges.,' vol. 65, p. 446 (1932). Fuchs and Donle, *loc. cit.*

† Cassie, 'Nature,' vol. 131, p. 438 (1933).

‡ Hare and Mack, 'J. Amer. Chem. Soc.,' vol. 54, p. 4272 (1932).

§ 'Phys. Z.,' vol. 33, p. 165 (1932).

|| Bergmann and Tschudnowsky, 'Ber. deuts. chem. Ges.,' vol. 65, p. 457 (1932).

¶ Watson, 'Proc. Roy. Soc.,' A, vol. 117, p. 43 (1927).

** Bergmann and Schütz, 'Z. phys. Chem.,' B, vol. 19, p. 401 (1932); Bergmann, Engel, and Sándor, 'Z. phys. Chem.,' B, vol. 10, p. 397 (1930).

†† Bergmann and Engel, 'Phys. Z.,' vol. 32, p. 507 (1931); Smith, 'Proc. Roy. Soc.,' A, vol. 136, p. 256 (1932).

‡‡ 'J. Amer. Chem. Soc.,' vol. 53, p. 1367 (1931).

The forces mentioned in (*b*) can be either interdipolar forces, which are much smaller in diphenyl methane than in the ethers or thioethers, or steric forces between the attached groups. The former, if purely electrostatic, are too small to produce the observed widening in oxygen unless at the same time the force constant resisting bending is much smaller in oxygen than in carbon or sulphur. Moreover, the angle is much the same in diphenyl methane as in diphenyl sulphide, although there must be a considerable difference in the electrostatic forces. If the change of angle is due to difference of steric effects, then a comparison of the spatial requirements of the phenyl groups in the methylene, oxygen, and sulphur compounds should be of value. Performing calculations similar to those of Smyth and Walls,* in order to ascertain the minimum angle at which the axes of the benzene rings would have to be in these compounds for the ortho hydrogen atoms just to clear when the rings are co-planar (taking distances $C_{al.} - C_{al.} = 1\cdot54$ A., $C_{ar.} - C_{ar.} = 1\cdot45$ A., $C - O = 1\cdot47$ A., $C - S = 1\cdot79$ A., $C - H = 1\cdot15$ A., and the nearest distance of approach of the *o-o'* hydrogen atoms as 0·75 A., the atomic diameter), we find that the angle is 121° in Ph_2CH_2, 124° in Ph_2O, and 111° in Ph_2S. If we assume that the electron repulsions of unlinked atoms can be roughly represented by an envelope 0·5 A. thick,† and the centres of the *o-o'* hydrogen atoms therefore only approach to within 1·75 A., then these angles are increased respectively to 142°, 146·5°, and 131°. There will be no tendency for the angles to be greater than this, and no necessity for them to be as great, because the molecule need not have the two rings co-planar as one of its normal phases, although thermal agitation will tend to promote this. It would appear, therefore, that in diphenyl ether there is complete freedom of rotation, in diphenyl methane rotation is considerably restricted, in that the rings can only rotate in phase, whilst in the sulphide it is not completely free but is more so than in diphenyl methane. Steric effects would not account for the large angles which we find in water and dimethyl ether. Again, Sidgwick (*loc. cit.*) has shown that the widening in diphenyl ether from this cause would only be possible if the force constant of deflection were very small.

Thus it is clear that differences of interdipolar forces if purely electrostatic, or of steric effects, cannot account alone for the differences of angle. They must be due mainly to difference either of natural angle, or of deflection force constant.

One objection to the latter factor alone being the main one, is that the force constant for oxygen would have to be very small, for which there is at present little evidence either way from infra-red or Raman spectra analysis or thermal data. Also it would suggest that the deflection force constant is greater for sulphur than for oxygen, which is opposed to the results, from spectral analysis, of Trumpy* and of Urey and Bradley† in an analogous series C, Si, Ti, Sn, and of Kohlrausch‡ in the series P, As, Sb, Bi.

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* 'J. Amer. Chem. Soc.,' vol. 54, p. 3230 (1932).

† Sidgwick, 'Ann. Rep. Chem. Soc.,' vol. 39, p. 72 (1932).

On the other hand, it is supported by the fact that the moments of the aliphatic ethers decrease with increase in the size of the alkyl group,§ as might be expected from steric effects, but the moments of the aliphatic thioethers increase with increasing alkyl group,|| which presumably is due to induction along the chain, without the corresponding widening of the angle.

The most acceptable generalization at present seems to be that the disposition of the single co-valencies about an atom depends upon the nature of its valency group of electrons, the electrons, whether shared or unshared, appearing to have definite spatial requirements. If there is a fully shared octet, as in the carbon compounds and the sulphones, the valencies are directed along the axes of a regular tetrahedron and show a large resistance to deformation. If there is a partially shared octet, as in the ethers, sulphides, and sulphoxides, the angles between the valencies increase, probably because of a decrease of the deformation force constants, this effect being less in sulphur than in oxygen. Finally, if there is an incomplete octet, the electrons dispose themselves as symmetrically as possible, a sextet giving a planar molecule, as in boron, and a quartet a linear one, as in mercury.¶

The authors desire to express their gratitude to Dr. N. V. Sidgwick for his invaluable advice, to the Department of Scientific and Industrial Research for grants which have enabled two of them (L. E. S. and G. C. H.) to carry out this work, and to Imperial Chemical Industries for a grant towards the cost of it.

Summary.

(1) From the electric dipole moments of diphenyl methane, diphenyl ether, diphenyl sulphide and their derivatives, the angles between the axes of the phenyl groups in these compounds have been found to be 115° ± 5°, 142° ± 8°,

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* 'Z. Physik,' vol. 66, p. 790 (1930).

† 'Phys. Rev.,' vol. 38 (ii), p. 1969 (1931).

‡ 'Phys. Z.,' vol. 32, p. 404 (1931).

§ Sänger, 'Helv. Phys. Acta II,' vol. 136 (1929).

|| Hunter and Partington, 'J. Chem. Soc.,' p. 2819 (1932).

¶ Krishnamurti, 'Nature,' vol. 125, p. 892 (1930); Dadieu and Kohlrausch, "Der Smekal-Raman Effekt," Berlin, 1931, p. 182.

and 118° ± 8° respectively. From data for anisoles and phenols, the angles in these have been estimated as 150° and 137° and the moments of the O–CH_3 and O–H links as 2·33 and 2·37 respectively. Application of these moments to dimethyl ether and water give angles in these latter compounds of 147° and 134°.

(2) Moments of diphenyl sulphoxide and its derivatives give the angles between each pair of valencies to be about 115°, and the moment of the $S \rightarrow O$ link to be 2·63.

(3) The significance of these results has been discussed.

The Influence of Pressure on the Spontaneous Ignition of Inflammable Gas-Air Mixtures. II.—*Pentane-Air Mixtures.*

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(Communicated by W. A. Bone, F.R.S. Received August 4, 1933).

Introduction.

In a recent communication* an account was given of an investigation into the influence of varying initial pressure on the spontaneous ignition of butane-air mixtures. Whereas at atmospheric pressure the known values of ignition temperatures for these mixtures were between *circa* 550 and 600° C. at higher pressures as, for example, those employed in the adiabatic compression method they had been located at *circa* 300° C.† By progressively increasing the pressure from atmospheric to 15 atmospheres we were able to show that the ignition points actually fell into two well-defined groups the one above 450° C. for pressures not exceeding about 3 atmospheres and the other below 370° C. for higher pressures. Transference of an ignition point from the higher to the lower group occurred at a definite critical pressure which depended upon the composition of the mixture.

This new feature of hydrocarbon combustion seemed of undoubted importance in regard to the phenomenon of "knock" in internal combustion engines, the more so when it was discovered that the presence of 0·05% of lead tetraethyl was capable at pressures near the critical transition pressure of raising

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* 'Proc. Roy. Soc.,' A, vol. 141, p. 484 (1933).

† *Cf.* also Berl, Heise and Winnacker, 'Z. phys. Chem.,' A, vol. 139, p. 453 (1928).

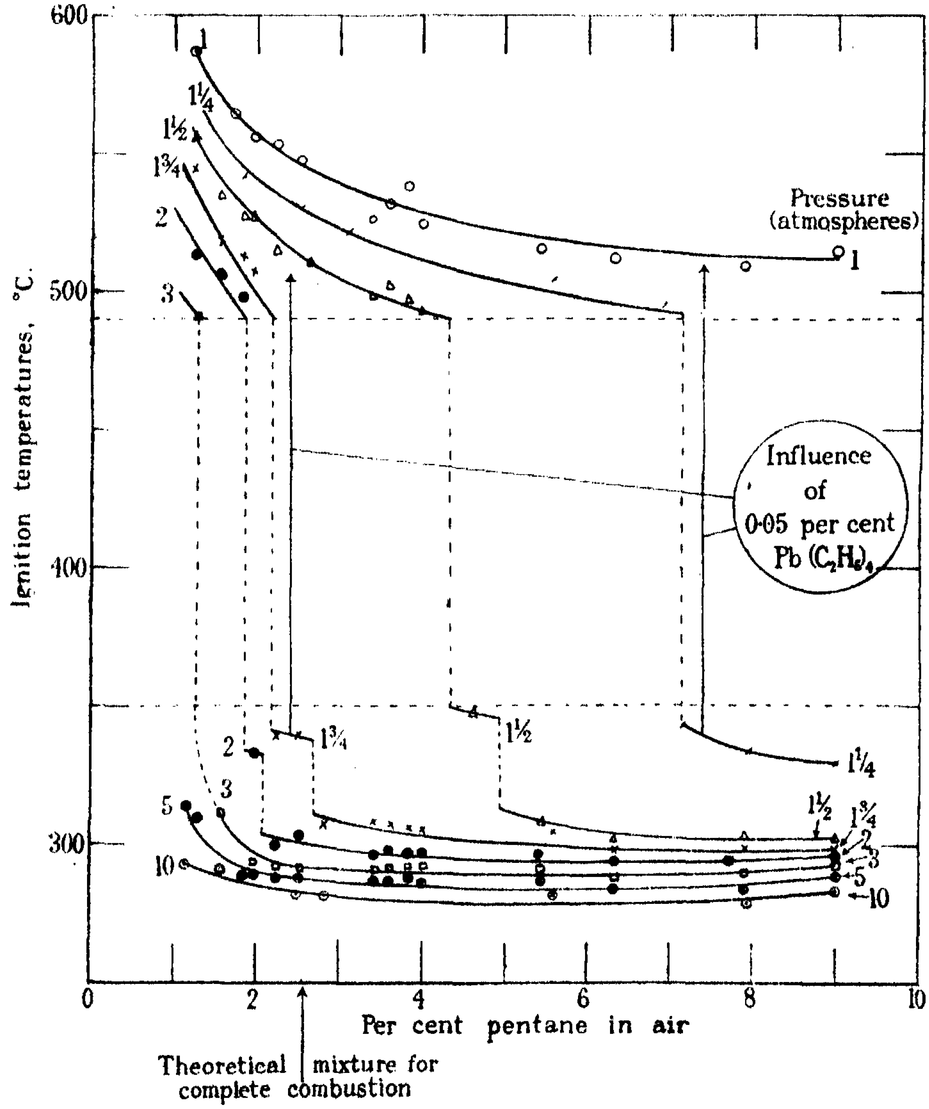

Fig. 1.

the ignition point from the lower to the higher group. On this account we have been determining the critical pressure regions in other explosive media and our results for pentane-air mixtures are incorporated in this paper.

Experimental.

In all essentials the experimental procedure was that previously employed (*q.v.*). Certain improvements in detail, resulting from experience gained as the investigation has proceeded, however, have enabled us (*a*) to achieve more rapid admission of the explosive media to the explosion vessel, and (*b*) gain closer observation of the characteristics of the ignitions.

The gas mixtures were made up and stored as before, measured quantities of *n*-pentane (boiling point 36–37° C.) being first placed in the storage cylinders and compressed air subsequently admitted as desired. Samples were taken from the cylinders both before the commencement and after the completion of a series of determinations and their composition checked by gas analysis.

Results.

Ignition Point Curves.—In fig. 1 we have plotted a series of curves showing the observed variation of ignition points with composition for mixtures of pentane contents between 1 and 9% and at pressures of 1, 1¼, 1½, 1¾, 2, 3, 5, and 10 atmospheres. These may be compared with the corresponding curves for butane-air mixtures (fig. 2, *loc. cit.*) attention being specially directed to the following observations:—

(1) The zone between the two groups of curves is wider for pentane (viz., 350° to 490°) than for butane-air mixtures (viz., 370° to 450°).

(2) Whereas a pressure of 1¾ atmospheres was necessary to lower the ignition point of butane-air mixtures containing more than 3·5% of the combustible from the higher to the lower group, for pentane-air mixtures containing more than (*a*) 7·0%, and (*b*) 4·3% of the combustible 1¼ and 1½ atmospheres, respectively, sufficed.

(3) With mixtures containing an excess of air conditions were found to be much the same for pentane-air mixtures as for butane-air mixtures. Thus with both gases 5 atmospheres pressure sufficed to lower the curve for all mixtures to the lower group while at 3 atmospheres pressure in both instances the ignition points only of very weak mixtures were still located in the higher group.

(4) A close examination of the ignition points at pressures near the critical transition pressure has shown the curves in the lower group to be discontinuous, breaks in them being indicated by dotted lines, a matter to which we shall refer in more detail.

(5) Just as the presence of 0·05% by volume of lead tetraethyl effected a transference of the ignition points of the 5 and 8% butane-air mixtures at 1¾ atmospheres pressure from the lower to the higher group, so a similar transference has been observed with two pentane-air mixtures selected at random and containing 2·4 and 7·4% of the combustible at 1¾ and 1¼ atmospheres, respectively (fig. 1), as the figures in Table I show.

Table I.

Initial pressure (atms.)	2·4% C_5H_{12}-air mixture.			7·4% C_5H_{12}-air mixture.		
	Normal ignition point ° C.	I.P. with 0·05% $Pb(C_2H_5)_4$ ° C.	Rise ° C.	Normal ignition point ° C.	I.P. with 0·05% $Pb(C_2H_5)_4$ ° C.	Rise ° C.
1	548	574	26	510	534	24
1¼	535	553	18	338	505	**167**
1½	512	538	26	305	333	28
1¾	338	509	**171**	300	307	7
2	298	343	45	292	300	8
3	292	298	6	288	292	4
5	288	293	5	285	289	4

The Critical Transition Pressures.—Our experiments with pentane-air mixtures had not proceeded far when we discovered that at pressures near the critical transition pressure ignition in the lower group might occur at first only over a limited temperature range. At temperatures above this another range was found in which ignition did not occur. Later at pressures still slightly higher we discovered two independent temperature ranges each covering a few degrees in which ignition occurred and outside of which it did not. We decided, therefore, thoroughly to investigate the matter, with results which have been very informative.

Curve 1, fig. 2, shows in detail for a 3·7% pentane-air mixture the influence on the ignition points of the first small pressure increases after the critical transition pressure had been reached. For clarity it should be noted that the heavy lined portions of the curve correspond with the ignition points plotted in fig. 1 and also that ignition always occurred at any temperature and pressure found in the area to the right of the curve.

At pressures between 1 and 1·55 atmospheres (the critical transition pressure) ignition occurred in the top group, the ignition points falling progressively from 532 to 490° C. At 1·55 atmospheres ignition also occurred at 350° C., but at temperatures between 350 and 490° C. the mixture was not ignitible. Increase of pressure from 1·55 to 1·65 atmospheres widened the lower ignition point range to temperatures between 340 and 363° C., and at the same pressure ignition became possible at 303° C. Still further increase in pressure created a second ignition point range; thus at 1·75 atmospheres ignition occurred at temperatures between 300 and 304° C., between 332 and 373° C. and finally at all temperatures above 445° C. At 1·9 atmospheres ignition occurred at all temperatures above 297° C. Thus over a small pressure range between 1·55 and 1·9 atmospheres in transference of the ignition points from the higher to the lower group they are located initially only within certain narrow temperature ranges.

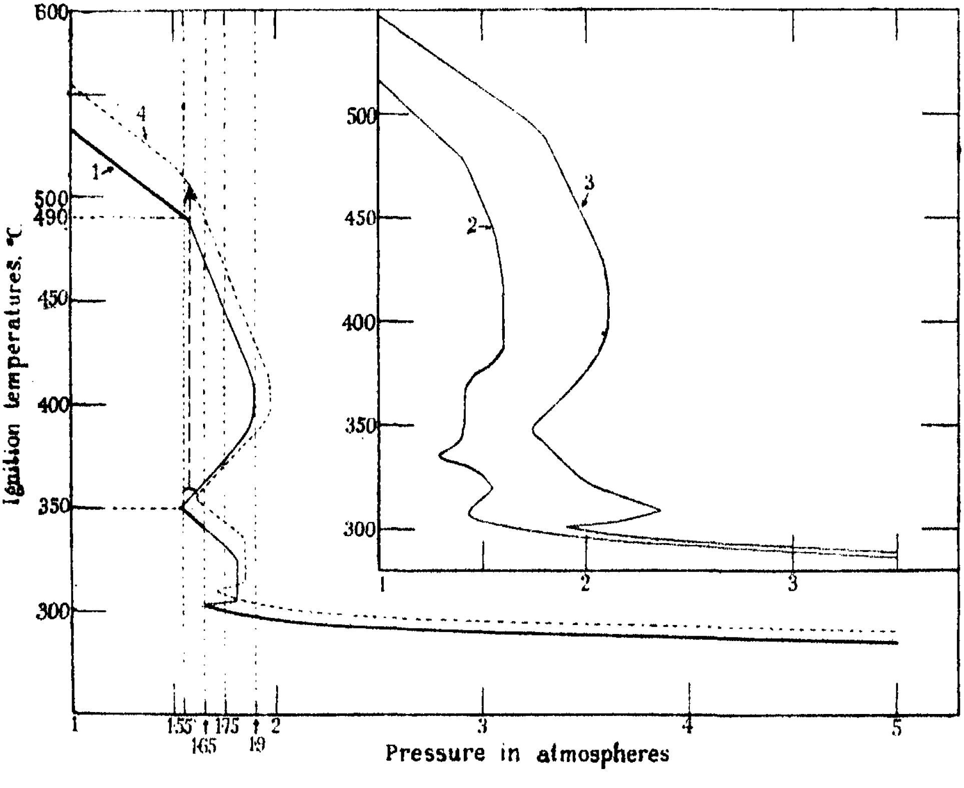

FIG. 2.—The percentage mixtures for the curves are 1 = 3·7; 2 = 6·9; 3 = 2·5; 4 = 3·7 with 0·1% Pb $(C_2H_5)_4$.

Curves 2 and 3 have been plotted similarly for 6·9 and 2·5% pentane-air mixtures and show similar features. In all three mixtures the incidence with increasing pressure of two widening ignition point ranges, which ultimately merge, at temperatures first between 335 and 350° C. and later between 300 and 308° C. is clearly manifest.

For the purpose of comparison we have also determined the corresponding curve for a 3·7% pentane-air mixture to which 0·1% of lead tetraethyl had been previously admixed (curve 4, dotted line). It would appear that the effect of an antiknock is almost uniformly to shift the curve towards the top right-hand corner of the diagram. In other words, when an antiknock is present, usually at any temperature a higher pressure or at any pressure a higher temperature is necessary for ignition. The effect in itself is small, but over a small pressure range the rise in ignition point (indicated by the arrow) becomes disproportionately great.

Cool Flames.—There exists considerable confusion in the literature owing to lack of proper discrimination among observers between true ignitions and what are usually described as cool flames. We wish to be clearly understood that the data presented in this communication refer solely to true ignitions. With the increased sensitiveness of our apparatus we have observed with pentane-air mixtures the development in certain circumstances of a small "pressure pulse." In other experiments in which we are collaborating with Mr. L. L. Cohen, M.Sc., we have identified this pulse with the appearance as seen through quartz windows of a slow-moving pale bluish flame which is accompanied by considerable formation of intermediate products strongly aldehydic in character.* True ignition, on the other hand, is marked by appreciable rapid pressure development and light emission and the combustion products contain merely traces of intermediate products.

The cool flames invariably made their appearance in our experiments when temperatures slightly higher than 300° C. had been attained and then after a considerable time-lag. This lag decreased so as to become very short as the temperature was raised; beyond 400° C. cool flames were no longer observable. Although they have been detected at all temperatures between 300 and 400° C. and at all pressures over this range true ignition occurred only under the limited conditions of temperature and pressure shown in figs. 1 and 2. There is no doubt, however, that the cool flames and true ignitions are related phenomena, for whenever true ignition occurred in the lower group of ignition points at temperatures between 300 and 350° C. it always followed instantly the appearance of a cool flame.

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* *cf.* Prettre, 'Bull. Soc. chim. Paris,' vol. 51, p. 1132 (1932).

Discussion.

The Role of Intermediate Compounds.—We think that the results so far obtained are best explained on the view previously put forward, namely, that the lower group of ignition points is the outcome of the rapid oxidation of certain intermediate oxygenated bodies whose survival is favoured by high pressure; the higher group results from ignitions of the products of their thermal decomposition which is favoured by low pressure. If this be so, the complete explanation of our observations will be forthcoming only from a knowledge of the rates of formation, decomposition, and further oxidation of intermediate products under like experimental conditions and of the part played by antiknocks thereon. It may be added, however, that evidence is accumulating that aldehydes and perhaps acetaldehyde in particular are likely to be the bodies most concerned, in which circumstance the view advanced by Bone and Hill* that their results indicated "the acetaldehyde stage of combustion as being probably important from the point of view of knock" will prove correct.

Acetaldehyde is a principal product in the oxidation of all higher normal paraffin hydrocarbons and the ignition points of its mixtures with air are known at temperatures of *circa* 300–350° C. Moreover, just as Bone and Hill showed the presence of 1% of acetaldehyde to cause the ignition of a $C_2H_6 + O_2$ mixture at 316° C. and 710 mm. pressure under conditions when normally the reaction proceeded quite slowly, so recently we have found the presence of small amounts of the aldehyde to lower the ignition points of a 3·5% pentane-air mixture from the upper to the lower group of ignition points as the preliminary figures in Table II show.

Table II.

Initial pressure (atms.)	Normal I.P. ° C.	CH_3CHO addition %	I.P. ° C.	Fall in I.P. ° C.
1·0	534	0·9	318	**216**
1·25	515	0·75	310	**205**
1·5	496	0·75	300	**196**
2·0	298	0·75	294	**4**

At 2 atmospheres pressure where the ignition point is normally in the lower group only a negligible effect is observed.

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* 'Proc. Roy. Soc.,' A, vol. 129, p. 434 (1930).

Knock.—It has been well appreciated, mainly as the outcome of the work of Tizard and Pye,[*] that there is a close relationship between both ignition points and temperature coefficients of reaction velocity of fuel-air media and their knocking propensities in an engine. There have been, however, certain practical difficulties to an unqualified acceptance of this relationship. Although our experiments are incomplete we think that they may ultimately go far to remove some of the difficulties referred to and would direct attention to the following :—

(1) The sudden fall in ignition point at the critical transition pressure corresponds with the incidence of knock in an engine on the attainment of a definite compression ratio.

(2) Mixtures containing excess of combustible are known to knock more easily than those with an excess of air ; in our experiments much less pressure is necessary to transfer to the lower group the ignition points of these mixtures than those of mixtures with an excess of air.

(3) The higher members of the paraffin hydrocarbons give rise to knock with less compression than do the lower ones. We have found the following pressures necessary to lower the ignition points of corresponding mixtures with air of the following hydrocarbons : propane (experiments not yet complete), 3 to 4 atmospheres ; butane, $1\frac{3}{4}$ atmospheres ; pentane, $1\frac{1}{4}$ atmospheres ; and hexane $1\frac{1}{10}$ atmospheres.

(4) The influence of an antiknock in practice is to enable the compression to be raised before knock occurs ; the increase in compression, however, is strictly limited. In our experiments an antiknock raises the ignition point from the lower to the higher group only over a small pressure range; at higher pressures the ignition point remains in the lower group almost unaltered.

(5) In certain instances raising the working temperature has been found actually to suppress knock.[†] We have observed temperature ranges in which ignition does not occur, although at lower temperatures it may do so.

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[*] 'Proc. N. E. Coast Eng.,' vol. 31, p. 381 (1921) ; Phil. Mag., vol. 44, p. 75 (1922) ; *ibid.* vol. 1, p. 1094 (1926).

[†] *Cf.* Fenning, 'Aero. Res. Ctee., Rep. and Mem.,' No. 979 (1925) ; also Egerton and Sates, *ibid.*, No. 1079 (1926).

Note added in Proof:—Quite recently Dumanois ('C.R. Acad. Sci. Paris,' vol. 197. p. 393 (1933)) has suppressed knock in a variable-compression engine by raising the working temperature above 340° C.]

We are extending our investigation over a wide range of explosive media, including those of aromatic and side chain hydrocarbons and are studying the respective influences of the successively formed intermediate products throughout the combustions under pressure.

In conclusion, we desire to express our thanks to the King Edward Memorial Society, C. P., and Berar, India, for a Fellowship which has enabled one of us (M. R. M.) to devote his whole time to the work.

Summary.

An investigation has been made of the influence of pressure on the spontaneous ignition of pentane-air mixtures. As with butane-air mixtures, previously reported, the ignition points were found to lie in two well-defined groups, one being now above 490° C. for pressures not exceeding 3 atmospheres and the other below 350° C. for higher pressures. Transference of the ignition points from the higher to the lower group occurred at a critical pressure; for rich mixtures this was located at 1¼ atmospheres. The presence of lead tetraethyl was again found to raise the ignition points from the lower to the higher group at pressures near the critical transition pressure; on the other hand, small amounts of acetaldehyde at all pressures above atmospheric lowered the ignition points to the lower group.

The bearing of these observations on the problem of knock is discussed.

Studies on the Formation of Complex Oxidation and Condensation Products of Phenols. A Contribution to the Investigation of the Origin and Nature of Humic Acid. Part I.—Studies of the Reactivity of Simple Monocyclic Quinones.

By H. G. H. **Erdtman.**

(Communicated by R. Robinson, F.R.S.—Received 27 January 1933. Revised 31 July 1933.)

In spite of numerous investigations the chemical nature of the humic acids remains obscure, and one result of the defects of our knowledge is the loose application of the term "humic acid" in the literature. For example, the definition given by S. Oden[†] in his excellent monograph, might also cover any "brown or brownish-black substance of unknown constitution."

It has long been known that oxidation of certain tannins and other phenolic compounds yields products (phlobaphenes) resembling humic acids, and it has been plausibly suggested that humic acids and these products of oxidation and condensation are chemically related.

Among the recent advocates of a carbocyclic structure for the humic acids may be mentioned Fischer and Eller. Fischer[‡] advanced the theory that humic acids arise from the aromatic constituents of plants. He considered that the most important source is lignin, the aromatic nature of which has been conclusively demonstrated by Klason and by Freudenberg.

Eller[§] pointed out the very close similarities between the "natural humic acids" and "artificial humic acids" obtained from different phenols on oxidation by persulphates in alkaline solution. The "humic acids" obtained from sugar when treated with strong acids behave in an entirely different manner and belong to a quite different series of compounds.[||]

Eller found that certain phenols when oxidized under varied conditions in alkaline solution yield a "humic acid" of constant composition. He assumed that the product thus obtained is a pure substance, and advanced the following scheme for the route of oxidation of the phenol to the humic acid :—

[†] "Die Huminsäuren," etc., Dresden, 1919, pp. 21 and 31.

[‡] 'Brennst., Chemie,' vol. 2, p. 37 (1921).

[§] 'Ber. deuts. chem. Ges.,' vol. 53, p. 1473 (1920); 'Liebig's Ann.,' vol. 431, p. 133 (1923); vol. 442, p. 160 (1925).

[||] Compare Eller, *loc. cit.* (1923); Marcusson, 'Ber. deuts. chem. Ges.,' vol. 58, p. 869 (1925); Komatsu and Tanaka, "The Sexagint," Kyoto, 1927, pp. 1 and 13.

$$\begin{tikzcd}
\text{Quinol} \arrow[r] & \text{Hydroxyquinol} \arrow[r] & \text{Hydroxyquinone} \arrow[r] & \text{Humic acid} \\
\text{Catechol} \arrow[ru] & \text{Quinone} \arrow[ru] & &
\end{tikzcd}$$

The empirical composition of the humic acid is given by Eller as ($C_6H_4O_3$)n, and the main feature of humic acid formation is regarded as the polymerization of hydroxyquinone by alkali. Hydroxyquinone was prepared by Willstätter and Müller,[†] and was indeed found to be extremely unstable and prone to polymerize.

Eller's theory is supported by the following facts. The humic acids exhibit quinonoid properties, for example they decompose phenylhydrazine carbamate.[‡] The colour of several (terphenyl-) hydroxyquinones is dark brown.[§] The humic acids, when freshly prepared and not dried, easily undergo reduction to leuco-compounds.[||] By reductive acetylation, stable "leuco"-acetates are formed (compare IV, p. 236). The acidic properties of humic acids are easily explained on this theory, since hydroxyquinones are, in general, strong acids. Nearly all quinones (not all hydroxyquinones) are extremely sensitive towards alkali, and the products obtained by treatment with alkali exhibit all properties of humic acid.

The conversion of phenolic compounds into humic acids may be accomplished by simple "autoxidation" by means of the oxygen of the air or by the action of enzymes. Therefore the study of the autoxidation of phenols and their enzymatic dehydrogenation should provide us with valuable models of the processes of formation of natural humic acids. With reference to previous work, it will suffice here to refer to the schemes of electro-chemical oxidation put forward by Fichter.[¶]

Quinones as well as phenols may undergo nuclear coupling, and a well-known example is the conversion of β-naphthoquinone in the presence of hydrogen ions into a derivative of the di-β-naphthoquinol series.

The phenols having the greatest interest in connection with humic acids are those belonging to the catechol, quinol, hydroxyquinol and pyrogallol series, which may be converted into quinones. In Eller's schemes the essential stage is the polymerization of a quinone, and it is important to elucidate the sequence of events when known quinones "polymerize."

[†] 'Ber. deuts. chem. Ges.,' vol. 44, p. 2180 (1911).

[‡] Willstätter and Cramer, 'Ber. deuts. chem. Ges.,' vol. 43, p. 2979 (1911).

[§] Pummerer and co-workers, 'Ber. deuts. chem. Ges.,' vol. 55, p. 3113 (1922); vol. 60, p. 1442 (1927).

[||] Erdtman, 'Svensk. kem., Tidskr.,' vol. 38, p. 205 (1926).

[¶] *Cf.* 'J. Soc. Chem. Ind.,' vol. 48, pp. 325, 341 (1929).

The present investigation is part of an attempt to follow the oxidative polymerization of certain phenols in the earlier stages, to isolate definite intermediate compounds, and to elucidate their constitution; little attention is paid to higher *amorphous* products. A detailed study of the reactivity at each stage must yield valuable information regarding the further polymerizations which are not so readily directly investigated.

The present communication deals, therefore, with the reactions of some of the simpler monocyclic quinones.

On the basis of the formula for benzoquinone proposed by Fittig,[†] Thiele[‡] put forward a partial valency formula later modified by Posner,[§] but although these structures explain satisfactorily most of the reactions of the quinones, the influence of substituents on the reactivity of the nucleus may be better understood on the basis of the electronic theory of valency.[||]

According to Lapworth[¶] and Robinson[††] the reactivity of unsaturated systems is due to their ability to become polarized. Polarization produces positive (kationoid), or negative (anionoid) centres, which facilitate the attack of (polarized) reagents of opposite electrochemical character.[‡‡] *p*-Benzoquinone may be regarded as composed of two katio-enoid systems of the $O{=}C{-}C{=}C{-}$ type (I). The effect of substituents on the reactivity of the quinone nucleus must depend on their influence on the polarization of the attached conjugated systems.

In order to study the reactivity of quinones systematically it was necessary to select a reagent which reacts smoothly with quinones without formation of by-products which complicate the interpretation of the results.

The most generally useful reagent is a mixture of acetic anhydride and sulphuric acid, which converts quinones into acetates of hydroxyquinols.

Without discussing the intimate mechanism of the process, it will suffice to regard the reaction as a simple addition of acetic acid to the quinone (II).

[†] *Cf.* Garner and Sugden, 'J. Chem. Soc.,' p. 2877 (1927).

[‡] 'Liebig's Ann.,' vol. 306, p. 132 (1899).

[§] 'Liebig's Ann.,' vol. 336, p. 85 (1904).

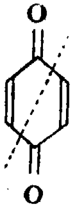
[||] Lewis, 'J. Amer. Chem. Soc.,' vol. 38, p. 762 (1916); Sidgwick, "The Electronic Theory of Valency," 1929.

[¶] 'Nature,' vol. 115, p. 625 (1925).

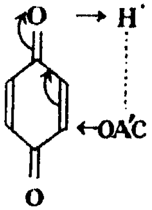
[††] *Cf.* 'J. Chem. Soc.,' p. 401 (1926).

[‡‡] For the application of this theory to quinonoid systems, compare Erdtman, 'Svensk. kem. Tidskr.,' vol. 45, p. 135 (1932).

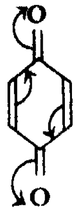
The transformation of the adduct to the benzenoid form may follow immediately the attachment of the acetoxy-group or, more probably, the introduction of the acetoxy-group, and the expulsion of a proton may proceed simultaneously and be of an oscillatory character.† The effects of substituents on the reactivity of some quinones and the position and the relative strength of the "partial valencies" will now be discussed.



(I)

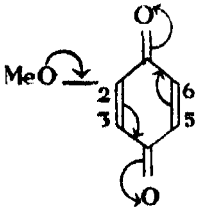


(II)

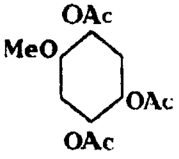


(III)

p-Benzoquinone (III) is symmetrical. It should be noted that the competition between the two carbonyl oxygen atoms as regards the polarization of the carbon double bonds hampers their tendency or ability to become polarized, and it is therefore not possible to locate any separate kationoid centre; the whole nucleus is of a diffuse kationoid character. Hence, in view of this dissipation of primary effects, it is not surprising that *p*-benzoquinone



(IV)



(V)

is a rather stable quinone. Strong acids are needed to effect polymerization, and the speed of reaction is not very great. The Thiele acetylation,‡ however, proceeds smoothly and hydroxyquinol triacetate is obtained in over 90% yield. Benzoquinone is instantly attacked by alkali yielding quinol and an amorphous substance "quinone humic acid."§

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† *Cf.* Bradley and Robinson, 'J. Chem. Soc.,' p. 1314 (1928).

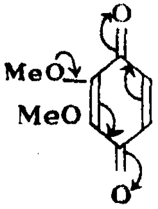
‡ For the sake of convenience this term is adopted for the reaction of quinones with acetic anhydride and sulphuric acid.

§ Hesse, 'Liebig's Ann.,' vol. 220, p. 367 (1883); Zincke and Hebrebrand, 'Ber. deuts. chem. Ges.,' vol. 16, p. 1555 (1883); Euler and Bohlin, 'Z. phys. Chem.,' vol. 66, p. 75 (1909); *cf.* Part III.

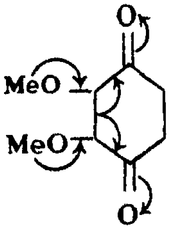
Methoxyquinone (IV) is asymmetrical. One of the conjugated systems is neutralized. The electron demand of the carbonyl oxygen constituting the negative end of the neutralized system is satisfied by the methoxyl oxygen at the other end. The second carbonyl oxygen satisfies its electron avidity from the 5 : 6-double bond, and in attracting electrons it creates a marked deficit at the carbon atom 5.

In accordance with this condition, methoxyquinone is an extremely reactive quinone. Thiele acetylation takes place almost instantly, giving a nearly quantitative yield of 2 : 4 : 5-triacetoxy-1-methoxybenzene (V). Methoxyquinone is extremely sensitive to acids and the couples in the 5-position to form 4 : 4′-dimethoxy-" diquinhydrone " (*cf.* Part II). The quinone is immediately polymerized by alkali.

2 : 3-Dimethoxyquinone† is more stable than methoxyquinone. Acids bring about slow polymerization to brownish, amorphous substances, and alkali decomposes it instantly. In general reactivity it seems to lie between *p*-benzoquinone and methoxyquinone. The writer is much indebted to Dr. W. Baker for a sample of this quinone.



(VI)



(VII)

In 2 : 3-dimethoxyquinone we may expect frequent phases of the type (VI) and hence a reactive 5-position. Actually this quinone does add the elements of acetic acid when treated with the Thiele reagent and gives 1 : 2 : 5-triacetoxy-3 : 4-dimethoxybenzene in very good yield. The phase (VII) may also occur in 2 : 3-dimethoxyquinone, but its frequency may be reduced owing to the crossing of the paths of transmission of the electron displacements in the neutralized systems. The occurrence of the phase may at least partly account for the fact that 2 : 3-dimethoxyquinone is more stable than methoxyquinone.

2 : 6-Dimethoxyquinone is remarkably inert, and the lack of reactivity is not easy to understand. At least one of the conjugated systems is neutralized

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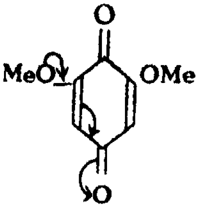
† Baker and Smith, 'J. Chem. Soc.,' p. 2547 (1931).

(VIII), but the other system should be weakly active according to the scheme (IX). That this is not so may be the result of the neutralization of the lower carbonyl group by both methoxyls diminishing unsaturation in the nuclear double bonds and hence making activation of a katio-enoid system less probable. The cause of the phenomenon may also be sought in some steric effect.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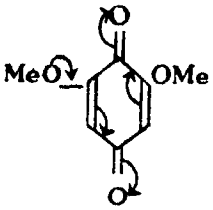
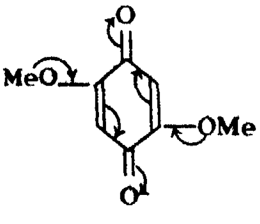

(IX)

2 : 6-Dimethoxyquinone does not react with the Thiele mixture even when exposed to it for six months at the ordinary temperature. At 80–100° the quinone is rapidly destroyed. Moreover, a more energetic reagent, namely, hydrogen chloride, is without influence. The quinone is also remarkably stable towards alkali. It is soluble in dilute aqueous alkalis, forming for a moment a colourless solution which, however, gradually becomes red. A freshly prepared solution, on acidification, deposits the unchanged quinone, but under the prolonged influence of alkali the quinone undergoes polymerization.† The solubility of a non-hydroxylated quinone in alkali is a rather surprising property. It is probably due to the formation of a complex addition compound, *e.g.*, $[C_6H_3(OCH_3)_2O(ONa)]OH$.


(X)

2 : 5-Dimethoxyquinone (X) is symmetrical, and both the conjugated systems are neutralized. As a consequence *p*-dimethoxyquinone does not react with the Thiele mixture. It is also quite stable towards hydrogen chloride and is

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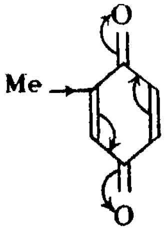
† Karrer, 'Helv. Chim. Acta,' vol. 13, p. 1424 (1930).

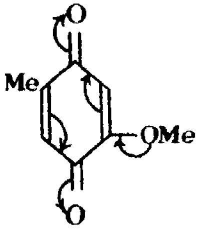
easily soluble in alkali *without polymerization.* Instead of causing polymerization, the alkali hydrolyses the methoxyl group yielding methyl alcohol and 2 : 5-dihydroxyquinone, which easily undergoes esterification to 2 : 5-dimethoxyquinone when dissolved in methyl alcoholic hydrogen chloride.†

2 : 5-Dimethoxyquinone may, in fact, be regarded as composed of two connected esterified carboxyl groups, each of which is extended by a —C=C— group.

Toluquinone (XI) is very similar to methoxyquinone, but far less reactive; it is, however, more reactive than *p*-benzoquinone. This is to be expected, as the low electron affinity of the methyl group enhances the frequency of the phase indicated in the above scheme.



(XI)



(XII)

Toluquinone undergoes the Thiele acetylation with great ease, and the yield of the 2 : 4 : 5-triacetoxy-1-methylbenzene formed in the reaction is very good.‡ Clark§ records that hydrogen chloride converts toluquinone chiefly into 4-chloro-2 : 5-dihydroxy-1-methylbenzene, and that the 3-chloro-isomeride is formed as a by-product. It is clear that these orientations are in harmony with theory.

2 : 6-Dimethylquinone (*m*-xyloquinone) exhibits certain analogies with 2 : 6-dimethoxyquinone. It undergoes the Thiele acetylation, however, although the reaction is much slower than for toluquinone. The reactivity of 2 : 6-dimethylquinone is even less developed than that of 2 : 5-dimethylquinone. This is of interest since 2 : 6-dimethoxyquinone seems to be more reactive than 2 : 5-dimethoxyquinone towards alkalis.

m-Xyloquinone is very stable towards acids. When dissolved in acetic acid and treated with concentrated sulphuric acid, it is slowly polymerized to a black amorphous product showing quinonoid properties.

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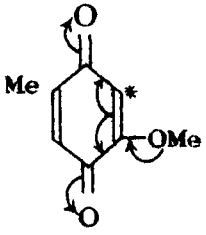
† Scholl and Dahl, 'Ber. deuts. chem. Ges.,' vol. 57, p. 81 (1925).

‡ Thiele and Winter, 'Liebig's Ann.,' vol. 311, p. 349 (1900).

§ 'J. Amer. Chem. Soc.,' vol. 14, p. 573 (1892).

2 : 5-Dimethylquinone (*p*-xyloquinone) has already been subjected to the Thiele acetylation by Asahina and Ishibashi,[†] and by Sonn.[‡] Since no direct comparison between the reactivity of 2 : 6- and 2 : 5-dimethylquinone is made possible by the statements in the literature, the Thiele acetylation of *p*-xyloquinone has been repeated. It was found unnecessary to leave the reaction mixture for 24 hours (Sonn). The reaction is completed in 10–15 minutes; under the same conditions *m*-xyloquinone reacted very incompletely. *p*-Xyloquinone and *m*-xyloquinone behave similarly in the polymerization with acids and alkali.

When methoxyl and methyl occur in the *para*-position to each other, we neutralize one of the conjugated systems of the quinone nucleus and obstruct the positive end of the other with a non-ionizable group.



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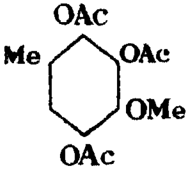


(XIV)

The phase represented by scheme (XII) should occur most frequently, but it cannot lead to reaction. The phase (XIII) (activation at *) may occur, although less frequently, because the carbonyl oxygen will encounter difficulties in attracting electrons fom the neutralized system.

The Thiele acetylation proceeds but slowly and furnishes 2 : 3 : 5-triacetoxy-4-methoxytoluene (XIV), obtained at once in an almost pure state and in quantitative yield. The proof of the constitution of this substance follows from its non-identity wih the isomeric 2 : 3 : 6-triacetoxy-4-methoxytoluene.[§]

Thiele (*loc. cit.*, p. 352), on treating 5-hydroxytoluquinone with acetic acid and sulphuric acid, obtained either 2 : 3 : 4 : 5- or 2 : 3 : 4 : 6-tetra-acetoxytoluene. The present author has repeated this experiment, hydrolysed the product and methylated the phenol. The product of the Thiele acetylation of 5-methoxytoluquinone was also hydrolysed and the phenol methylated.

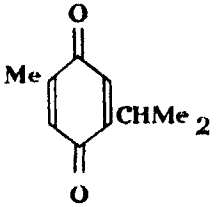
[†] 'Ber. deuts. chem. Ges.,' vol. 62, p. 1207 (1929).

[‡] 'Ber. deuts. chem. Ges.,' vol. 64, p. 1848 (1931).

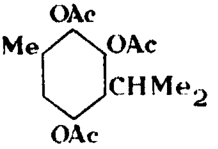
[§] Konya, 'Mhft. Chem.,' vol. 21, p. 431 (1900).

The two tetramethyl derivatives are identical, and hence the phenol obtained by Thiele was 2 : 3 : 4 : 5-tetrahydroxytoluene.

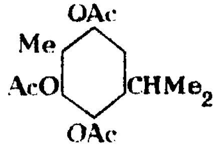
The interest of a study of the Thiele acetylation of thymoquinone (XV) lies in the analogy of this quinone with 5-methoxytoluquinone. The *iso*propyl group, by possessing a greater polar effect than the methyl group,[†] should facilitate the introduction of the acetoxy-group in the same position as does the methoxy group in 5-methoxytoluquinone. Thus thymoquinone should yield more XVI than XVII. An exclusive formation of the first substance is improbable, since the alkyl group lacks free electrons and the " neutralization " is consequently incomplete. Actually a mixture of the two substances was obtained, and the expected isomeride was isolated in the higher yield (about 60%). The structure of the main product was proved by independent synthesis from carvacrol as follows: dinitrocarvacrol; diaminocarvacrol; oxidation to 6-hydroxythymoquinone; and finally reductive acetylation. In a similar manner the isomeride obtained in smaller relative amount was synthesized from thymol.



(XV)



(XVI)



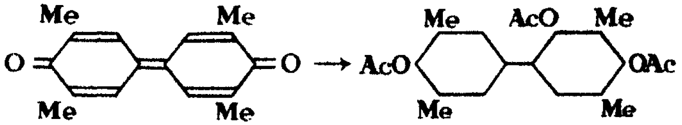
(XVII)

In the preceding discussion of the reactivity of the quinone nucleus we have considered the influence of groups having a smaller electron affinity than hydrogen. Turning now to the groups possessing a greater electron affinity than hydrogen (*e.g.*, COOH, CN, NO_2), we find that such quinones in general are not stable. " Quinone carboxylic acid," " Cyanoquinone " and " Nitroquinone " do not exist. The corresponding phenols either do not undergo oxidation or " decompose." A group having a greater electron avidity than hydrogen cannot " neutralize " any conjugated system of the quinone nucleus; on the contrary, it increases the strength of the kationoid centre in the ortho-position. Reactions supporting this view are, for example, the addition of hydrogen cyanide to benzoquinone with formation of *o*-dicyanoquinol[‡]; the addition of hydrogen cyanide to quinone carboxylic acid methyl ester[†]: the oxidation of 2-nitro-4-aminophenol.[‡]

[†] Robinson and co-workers, ' J. Chem. Soc.,' pp. 376, 392, 406 (1926).

[‡] Thiele and Meisenheimer, ' Ber. deuts. chem. Ges.,' vol. 33, p. 675 (1900); Thiele and Günther, ' Liebig's Ann.,' vol. 349, p. 50 (1906).

In this connection it is of some interest that the present author has found that a number of the highly active diphenoquinone group, 3 : 5 : 3′ : 5′-tetramethyldiphenoquinone, easily yields 2 : 4 : 4′-triacetoxy-3 : 5 : 3′ : 5′-tetramethyldiphenyl when submitted to Thiele acetylation.



The results discussed above are of a qualitative character, but they serve to show the order of reactivity of the respective quinones. The author is continuing the work in the direction of kinetic studies of the Thiele acetylations.

EXPERIMENTAL.

Methoxyquinol.—This phenol was obtained from vanillin and hydrogen peroxide[§] (yield 70–73%). The *diacetate*, needles, m.p. 95–96°,[||][¶] obtained, by heating the phenol with acetic anhydride and pyridine, was recrystallized from methyl alcohol (found: MeO, 14·0. Calc. for $C_{10}H_9O_4OMe$. MeO, 13·8%).

Methoxyquinone.—Dry methoxyquinol (7 gm.) was dissolved in hot, dry benzene (150 c.c.), anhydrous magnesium sulphate (15 gm.) and lead peroxide (50 gm.) were added and the whole shaken vigorously. The benzene almost immediately acquires a yellow colour, and on evaporation of a sample a violet quinhydrone is formed. In order to complete the oxidation, the mixture is refluxed on the steam bath and frequently shaken. When a sample of the solution deposits pure yellow or only faintly greenish crystals on evaporation, the solution is filtered from the lead sludge. This is extracted with boiling benzene (100 c.c.) and the combined filtrates evaporated. The crude quinone (5 gm.) was recrystallized from amyl alcohol and the product (3·5–4 gm.) washed with a little methyl alcohol, m.p. 143–144°. Will,[††] who prepared this quinone in a different way, records m.p. 140°. Gomberg and Stone[†] give m.p. 145°.

[†] Brunner, 'Mhft. Chem.,' vol. 34, p. 919 (1913).

[‡] Kehrmann and Idzkowska, 'Ber. deuts. chem. Ges.,' vol. 32, p. 1065 (1899).

[§] Dakin, 'J. Amer. Chem. Soc.,' vol. 42, p. 496 (1909).

[||] *Cf.* Moore, 'J. Chem. Soc.,' vol. 99, p. 1045 (1911).

[¶] All melting points in this and the following papers are uncorrected. Most of the analyses were macro-analyses (F. Hall, Oxford); some were micro-analyses (Schoeller, Berlin).

[††] 'Ber. deuts. chem. Ges.,' vol. 21, p. 381 (1888).

2 : 4 : 5-*Triacetoxy*-1-*methoxybenzene* (V).—Methoxyquinone (5 gm.) was slowly introduced into acetic anhydride (30 c.c.) containing 2% of its weight of sulphuric acid. The quinone dissolved and its colour disappeared almost instantly. After 5 minutes the mixture was poured into a large quantity of water, and the acetate separated in colourless needles (yield 98–99%), recrystallized from acetic acid and from methyl alcohol m.p. 142° (found : MeO, 11·1. $C_{12}H_{11}O_6$. OMe requires MeO, 11·0%). The acetate was hydrolysed with methyl alcoholic sulphuric acid in an atmosphere of hydrogen, and the phenol methylated according to Chapman, Perkin and Robinson[‡]; 1 : 2 : 4 : 5-tetramethoxybenzene, m.p. 103°, was obtained in 95% yield. Schüler[§] records the m.p. 102·5°. It was easily oxidized by nitric acid to 2 : 5-dimethoxyquinone, and this quinone when treated with the Thiele reagent or hydrogen chloride in acetic acid or chloroform, did not react in six months; 2 : 6-dimethoxyquinone behaved similarly.

An attempt was made to add hydrogen chloride to methoxyquinone in different solvents; the product of reaction was always 4 : 4′-dimethoxy-"diquinhydrone" (*cf.* II, p. 211). Acetyl chloride gave the same product, but more slowly.

1 : 2 : 3-*Triacetoxy*-3 : 4-*dimethoxybenzene.*—2 : 3-dimethoxyquinone (0·3 gm.) was dissolved in cold acetic anhydride (9·5 c.c.) and sulphuric acid (0·5 c.c.), and after 24 hours the mixture was poured into water. An oil separated and soon crystallized in colourless prisms (yield, 0·35 gm. of m.p. 93–94°). After one crystallization from dilute acetic acid and distillation in high vacuum the m.p. was 96–97° (found : C, 53·8; H, 5·0. $C_{14}H_{16}O_8$ requires C, 53·8; H, 5·1%). The acetate dissolved in sulphuric acid to a yellow solution; it is easily hydrolysed by alkali yielding a violet solution.

2 : 4 : 5-*Triacetoxy*-1 : 3-*dimethylbenzene.*—*m*-Xyloquinone (15 gm.) was introduced during 30 minutes into a mixture of acetic anhydride (95 c.c.) and concentrated sulphuric acid (5 c.c.) at 40–50°, and then kept for 24 hours. After addition to water (800 c.c.) the oil solwly solidified and was collected and washed with water (yield, 28·5 gm. or 92%). Crystallization from 50% methyl alcohol furnished colourless, rectangular plates, m.p. 103–104°. Fittig and Siepermann[||] record m.p. 99°. A repetition of their work, however, yielded a

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[†] 'J. Amer. Chem. Soc.,' vol. 38, p. 1587 (1916).

[‡] 'J. Chem. Soc.,' p. 3028 (1927).

[§] 'Arch. Pharm. Berl.,' vol. 245, p. 281 (1907).

[||] 'Liebig's Ann.,' vol. 180, p. 37 (1876).

product having the higher melting point. When the two preparations were mixed no depression of the m.p. was observed.

2 : 3 : 5-*Triacetoxy*-1 : 4-*dimethylbenzene.*—*p*-Xyloquinone was subjected to Thiele acetylation in the same way as *m*-xyloquinone. After 15 minutes at 40–50° the mixture was poured into water, and the product of reaction (30 gm. or 96%) crystallized almost at once. Crystallized from aqueous acetic acid it formed white needles, m.p. 110° (Sonn, *loc. cit.*, records 109–110°).

5-*Methoxytoluquinone.*—This quinone was prepared from homoveratrole following the method of Luff, Perkin and Robinson.[†] Homoveratrole was easily obtained in 60% yield by Clemmensen reduction[‡] of veratraldehyde.

2 : 3 : 5-*Triacetoxy*-4-*methoxytoluene.*—A suspension of 5-methoxytoluquinone (5 gm.) in a mixture of acetic anhydride (50 c.c.) and sulphuric acid (2·5 c.c.) was allowed to stand at the ordinary temperature for 2 days and shaken occasionally; it was then poured into water and worked up as usual. The yield of 2 : 3 : 5-triacetoxy-4-methoxytoluene was quantitative, and the m.p. of the crude substance was 88–89°. After two crystallizations from dilute acetic acid long, prismatic needles, m.p. 91–92°, were obtained (found: C, 56·9; H, 5·1. $C_{14}H_{16}O_7$ requires 56·8; H, 5·4%).

2 : 3 : 4 : 5-*Tetramethoxytoluene.* — 2 : 3 : 5-Triacetoxy-4-methoxytoluene (10 gm.) was dissolved in hot 2% methyl alcoholic sulphuric acid (50 c.c.) and refluxed in an atmosphere of hydrogen for half an hour. The sulphuric acid was then neutralized with the calculated quantity of sodium hydroxide in concentrated solution, and the phenol methylated by means of methyl sulphate and sodium hydroxide in the absence of air. The methyl ether (yield, 85–90%) recrystallized in hexagonal plates, but was purified by distillation (m.p. 51–52°) (found: C, 62·0; H, 7·4. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5%). This substance has a burning taste and an odour similar to that of pyrogallol trimethyl ether.

Similarly, the tetra-acetate obtained by Thiele and Winter (*loc. cit.*) from 5-hydroxytoluquinone was hydrolysed and the phenol methylated. The two preparations were found to be identical, and mixed melting points showed no depression.

3-*Chloro*-2 : 5-*diacetoxy*-4-*methoxytoluene.*—5-Methoxytoluquinone was suspended in an excess of acetyl chloride to which a little acetic acid had been added, and after a day the liquid was poured on crushed ice. The chloroacetate was obtained as an oil which soon solidified. It was recrystallized from acetic acid and formed colourless needles, m.p. 126° (found; Cl, 13·2. $C_{12}H_{13}O_5Cl$ requires Cl, 13·0%). The structure of this compound is assigned from analogy with the product of Thiele acetylation of 5-methoxyquinone.

[†] 'J. Chem. Soc.,' p. 1137 (1910).

[‡] 'Ber. deuts. chem. Ges.,' vol. 47, p. 51 (1914).

During attempts to synthesize some halogenated compounds of the same type, an interesting example of abnormal bromination was noted. Creosol when brominated in acetic acid solution yields a monobromocreosol which is not the expected 5-bromocreosol (bromine *ortho* to the hydroxyl), but 6-bromocreosol (bromine *para* to the methoxyl). The structure follows from its conversion into 6-bromohomoveratrole on methylation and the nitration of the latter to 6-nitrohomoveratrole.†

6-*Bromocreosol.*—A solution of bromine (6·6 c.c.) in glacial acetic acid (50 c.c.) was slowly added to a cooled solution of creosol (20 gm.) in acetic acid (50 c.c.). The bromine was decolorized almost instantly, and the reaction mixture was poured into water (500 c.c.). The product (25 gm.) separated as an oil which soon solidified, forming needles or rhombic prisms, m.p. 82–83°, b.p. 270–275° with slight decomposition at the ordinary pressure (found: Br, 37·1. $C_8H_9O_2Br$ requires Br, 36·7%).

6-*Bromohomoveratrole.*—Methyl sulphate (1·5–2 mols.) was added to 6-bromocreosol (1 mol.) dissolved in 1½ times its weight of alcohol; the corresponding amount of 40% aqueous sodium hydroxide was then added in small portions to the stirred solution, and after the main reaction the mixture was rendered strongly alkaline and the bromohomoveratrole isolated by means of ether. The homoveratrole was purified by distillation, b.p. 265–267° (Jones and Robinson, *loc. cit.*, record b.p. 267°). On cooling in a freezing mixture, the oil solidified, m.p. 35–36°. On nitration with nitric acid in acetic anhydride, 6-nitrohomoveratrole needles, m.p. 121° was obtained (literature, m.p. 121°).

Thiele Acetylation of Thymoquinone.—Thymoquinone (5 gm.) was gradually added to a mixture (33 c.c.) of acetic anhydride and sulphuric acid containing 5% of the latter. The temperature was maintained at 40–50° throughout the reaction.

After 30 minutes, the reaction mixture was poured into water (500 c.c.), and the oil which separated gradually solidified on seeding (yield, 8·7 gm. or 93%). The substance sintered at 82° and fused at 111–115°.

Fractional crystallization of the mixture from ethyl alcohol yielded 3·3 gm. (38%, calculated on the 8·7 gm.) of a substance A, m.p. 86–87°, and 5·0 gm.

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† Jones and Robinson, 'J. Chem. Soc.,' vol. 111, p. 919 (1917); Heap, Jones and Robinson, 'J. Chem. Soc.,' p. 2022 (1927).

(57%) of a substance B, m.p. 135–137° (loss 4–6%). After exhaustive purification of the fractions (crytallizations from acetic acid involving great losses), the m.p. of A was 87–88° and that of B, 136–137° (found for A: C, 62·4; H, 6·5; for B: C, 62·4; H. 6·7. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5%).

2 : 3 : 6-*Triacetoxy*-1-*methyl*-4-*isopropylbenzene.* — 3-Hydroxythymoquinone† was subjected to reductive acetylation by short heating on the steam-bath with a mixture of acetic anhydride, acetic acid and zinc dust. When the quinone was decolorized the liquid was poured into water and the product worked up as usual. In an impure condition the substance crystallizes with difficulty, but from methyl alcohol it separated in needles, m.p. 87–88° (found: C, 62·5; H, 6·5. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5%). A mixed melting point with substance A showed no depression, with B sintering occurred from 83–120°.

2 : 3 : 5-*Triacetoxy*-1-*methyl*-4-*isopropylbenzene.* — 6-Hydroxythymoquinone‡ was subjected to reductive acetylation. The reaction product crystallized more readily than the isomeride and separated from methyl alcohol in needles, m.p. 137–138° (found: C, 62·4; H, 6·6. $C_{16}H_{20}O_6$ requires C, 63·3; H, 6·5%). A mixed melting point with substance B showed no depression.

2 : 4 : 4′-*Triacetoxy*-3 : 5 : 3′ : 5′-*tetramethyldiphenyl.* — The tetramethyldiphenoquinone was prepared in accordance with the method of Auwers and Markovits§ from *vic*-xylenol.

The Thiele acetylation was accomplished in the same manner as that of methoxyquinone. The marked red colour of the quinone rapidly disappeared, and when the solution was colourless, it was poured into water and the acetate worked up in the usual way. After recrystallization from methyl or ethyl alcohol, white needles, m.p. 141–142°, were obtained (found: C, 68·9; H, 6·2. $C_{22}H_{24}O_6$ requires C, 68·8; H. 6·3%).

Summary.

An attempt has been made to discusss the reactivity of quinones from the general standpoint of the electronic theory of valency.

The action of mixed acetic anhydride and sulphuric acid on quinones has been chosen as a standard reaction for the comparative study of the reactivity of simple quinones. This reaction has been applied systematically to methoxyl-substituted and methyl-substituted quinones of varied constitution.

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† Carstajnen, 'J. prakt. Chem.,' vol. 15, p. 398 (1877).

‡ Mazzara, 'Ber. deuts. chem. Ges.,' vol. 23, p. 1392 (1890).

§ 'Ber. deuts. chem. Soc.,' vol. 38, p. 226 (1905).

The nucleus of *p*-benzoquinone possesses a diffuse kationoid character.

Methoxy-quinone and methyl-quinone are highly reactive in the 5-position owing to the more or less complete neutralization of the conjugated system to which the substituent is attached.

2 : 3-Dimethoxyquinone is less active than methoxyquinone; 2 : 6- and 2 : 5-dimethoxyquinones possess little or no reactivity at the unsubstituted nuclear atoms; 2 : 6- and 2 : 5-dimethylquinones have active nuclear carbon atoms due to the incomplete power of neutralization of alkyl groups in comparison with alkoxyl groups.

5-Methoxytoluqinone is reactive in the 6-position, but the reactivity is weaker than that of *p*-xyloquinone.

Thymoquinone is approximately as reactive as *p*-xyloquinone. The greater polar effect of the *iso*propyl group compared with the methyl group enhances to some extent the reactivity of the 6-position.

Studies on the Formation of Complex Oxidation and Condensation Products of Phenols. Part II.—*Coupling of Simple Phenols and Quinones to Diphenyl Derivatives.*

By H. G. H. Erdtman.

(Communicated by R. Robinson, F.R.S.—Received 27 January 1932. Revised 31 July 1933.)

General.—The oxidative coupling of phenols with formation of diphenyl derivatives has long been known, but the mechanism of the reaction has not been discussed. On the basis of the Engler-Bach peroxide theory it seems possible to assume the intermediate formation of a peroxide, which would yield the diphenyl derivative by means of a rearrangement of the hydrazobenzene-benzidine type. There are, however, many objections to such a view. For example, it is characteristic of the benzidine migration that it takes place in the presence of acids. The oxidative coupling of phenols occurs readily in alkaline solutions also. The peroxides are known to dissociate into radicals containing monovalent oxygen,† and these radicals are very reactive and easily undergo spontaneous decomposition. On the other hand, the dissociation is reversible, and it seems to be more justifiable to regard the peroxide formation as an attempt by the free radicals to acquire stability, and to assume that the free radicals as such are responsible for the coupling of the phenols. Evidence in favour of this view has been provided by Pummerer† and his co-workers who have studied in particular the dehydrogenation of naphthols

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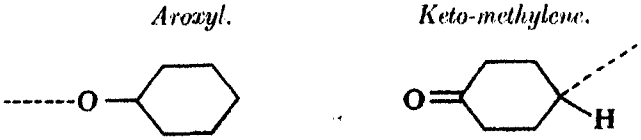
† Wieland, 'Ber. deuts. chem. Ges.,' vol. 44, p. 2551 (1911); Goldschmidt, 'Ber. deuts. chem. Ges.,' vol. 55, p. 3194 (1922).

That the "oxidation" of phenols is in reality a dehydrogenation has been conclusively demonstrated by Wieland, who discovered that phenols can easily be dehydrogenated to quinones or diphenyl derivatives by the action of platinum or palladium in absence of free oxygen.‡

Pummerer found it difficult to decide in many cases whether a dehydrogenation product was a monovalent oxygen radical or a tervalent carbon radical, and he observed properties characteristic of both types. He therefore assumed that the oxygen radical—the "aroxyl" is tautomeric with a "keto-methyl" radical as illustrated by the annexed scheme.§


Aroxyl. *Keto-methylene.*

(I)

This suggestion provides an explanation of the different coupling reactions often observed in phenol oxidation. When two "keto-methylene" radicals "collide," a diphenyl derivative is formed. When a keto-methylene and an aroxyl radical combine we obtain a phenol ether. The peroxide formation finally takes place when two aroxyls react with each other.||

On the basis of the electronic theory of valency the most important feature of the oxidation (dehydrogenation) of a monohydric phenol, for example, is the loss of one electron. (In quinone formation two electrons are taken up by the oxidizing reagent.) The unsaturated oxygen atom of the resulting radical by virtue of a strong positive charge will act as a powerful electron-seeking

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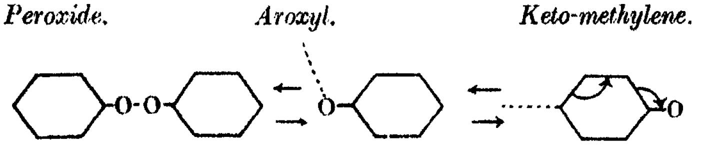
† 'Ber. deuts. chem. Ges.,' vol. 47, pp. 1472, 2957 (1914); vol. 52, pp. 1404 1414, 1416 (1919).

‡ *Cf.* Wieland, 'Ber. deuts. chem. Ges.,' vol. 55, p. 3639 (1922); 'Ergebn. Physiol.,' vol. 20, p. 477 (1922); Haber and Willstätter, 'Ber. deuts. chem. Ges.,' vol. 64, p. 2844 (1931).

§ 'Ber. deuts. chem. Ges.,' vol. 47, p. 1472 (1914).

|| *Cf.* further, Goldschmidt, Schultz and Bernard, 'Liebig's Ann.,' vol. 478, p. 1 (1930).

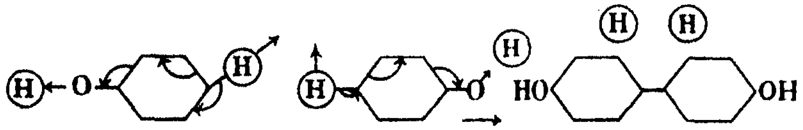
centre. On acquiring electrons from another aroxyl this radical undergoes polymerization to peroxide. The radical may, however, transfer electrons from the double bonds of the attached ring, and this results in keto-methylene formation.



(II)

In the latter the positive charge is transferred to the carbon atoms in the *ortho*- or *para*-positions, and the hydrogen atoms attached to these atoms may become ionized or transferred to the oxygen atom of another keto-methyl radical by means of a chain reaction.

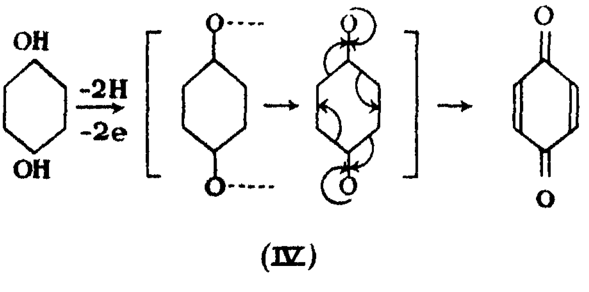
The electrons thus liberated effect the linking of the two nuclei:



(III)

Reactions of the same type are those of the photochemical dismutation of triphenylmethyl to bis-diphenylenediphenylethane and triphenylmethane† and the thermal decomposition of dianisylnitrogen into dianisylamine and dianisyldihydroanisazine.‡

In the dehydrogenation of a polyhydric phenol which is capable of quinone formation, we may assume the intermediate formation of a divalent radical, which isomerizes to the quinone:



(IV)

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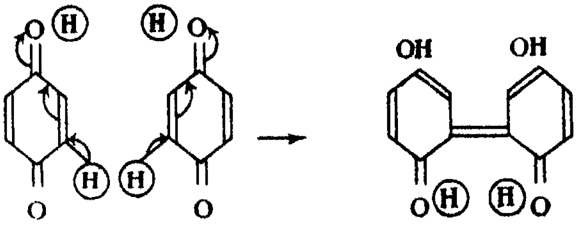
† Gomberg and Cone, 'Ber. deuts. chem. Ges.,' vol. 37, p. 493 (1904); Schmidlin and Garcia-Banus, 'Ber. deuts. chem. Ges.,' vol. 45, p. 1345 (1912).

‡ Wieland, 'Liebig's Ann.,' vol. 381, p. 200 (1911).

This by no means excludes the formation of intermediate meriquinonoid radicals as suggested by Haber and Willstätter (*loc. cit.*), and is in excellent agreement with the fact that Willstätter and Müller[†] have isolated a colourless peroxidic form of *o*-quinone which rapidly undergoes a rearrangement into the stable red one. In this connection it is of interest to recall that Euler and Brunius[‡] found that in dilute solutions the speed of oxidation of quinol to quinone depends upon the second dissociation constant of quinol. In other words, the ion $(C_6H_4O_2)$ seems to be directly converted into quinone by loss of two electrons.

If we now consider the question of the polymerization of quinones, *e.g.*, the conversion of β-naphthoquinone into the "quinhydrone" of di-β-naphthoquinone[§] or the coupling of methoxyquinone to 4 : 4′-dimethoxydi-"quinhydrone," which is described on p. 212, we find that this reaction occurs in acid solutions. In accordance with the views advanced for the addition reactions of quinones, such as the Thiele acetylations (see p. 180), we may assume the driving force of the reaction to be the addition of a proton to the carbonyl oxygen of the quinone.[‖] This addition is followed by the destruction of the double bond conjugated with the carbonyl group in question, thus causing an electron deficiency at the β-carbon atom and dissociation of the β-hydrogen. Coupling is then effected by means of the electrons liberated :



(V)

This explanation accounts for the fact that in the series benzoquinone, toluquinone, methoxyquinone, hydroxyquinone, the stability decreases and the power of coupling increases.

The Coupling of Pyrogallol to vic-*Dipyrogallol*.—The remarkable sensitivity of pyrogallol in akaline solution towards oxygen has engaged the interest of chemists for a century, but in spite of many investigations a true insight into the constitution of the brown amorphous acid formed in this reaction has not yet been reached. The present work was undertaken in order to try to isolate intermediate products of the oxidation and to elucidate their structure.

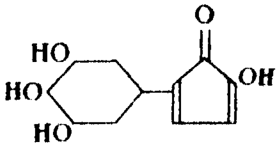
[†] 'Ber. deuts. chem. Ges.,' vol. 41, p. 2580 (1908).

[‡] 'Z. phys. Chem.' vol. 139, p. 615 (1928).

[§] Stenhouse and Groves, 'Liebig's Ann.,' vol. 194, p. 205 (1878).

[‖] In alkaline polymerization of quinones the kation of the alkali takes the place of the proton.

In approximately neutral solution pyrogallol is oxidized to purpurogallin, a substance which has been carefully investigated by Herzig and by Perkin. Ultimately the structure was elucidated in an indirect way by Willstätter and Heiss.† It appears that two molecules of pyrogallol are coupled asymmetrically to a hexahydroxydiphenyl, which is then oxidized to an ortho-quinone. This undergoes a migration of the benzil-benzilic acid type and yields purpurogallin VI :



(VI)

The oxidation is effected by a variety of agents—ferricyanides, nitrous acid, quinone or oxygen in presence of sodium phosphate or peroxidase, and finally dehydrogenation with palladium.

In strong alkaline or acid solution the oxidation takes different courses. In alkali the humic acid mentioned above‡ is formed.§

By the autoxidation of pyrogallol in baryta solution, Harries|| obtained a hexahydroxydiphenyl (hexa-acetate, m.p. 162–163°) which he believed to be an intermediate between pyrogallol and purpurogallin, but he did not succeed in preparing purpurogallin from this compound. Harries' dipyrogallol is not, in fact, an intermediate in the formation of purpurogallin (*cf.* Willstätter and Heiss, *loc. cit.*), but is to be regarded as the first stage of the oxidative polymerization of pyrogallol in alkaline solution.

Herzig, Pollak and Bronner¶ found that methyl gallate when shaken with aqueous ammonia or sodium carbonate solutions yields the dimethyl ester of ellagic acid. By fusion of ellagic acid with caustic potash, Barth and

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† 'Liebig's Ann.,' vol. 433, p. 17 (1923).

‡ Eller, 'Liebig's Ann.,' vol. 431, p. 160 (1923).

§ A bibliography has been compiled by Henrich, 'Z. angew. Chem.,' vol. 29, p. 149 (1916).

|| 'Ber. deuts. chem. Ges.,' vol. 35, p. 2954 (1902).

¶ 'Mhft. Chem.,' vol. 29, p. 277 (1908).

Goldschmidt[†] obtained a dipyrogallol which gave a characteristic blue colour with alkali (hexa-acetate, m.p. 170°). Sodium hydroxide, however, yielded a different product (alkali colour reaction, red; acetate, m.p. 163–164°); Cobenzl[‡] had earlier obtained a similar dipyrogallol by treating ellagic acid with sodium amalgam. By electrolytic reduction of ellagic acid in strong sodium hydroxide solution at 110°, Nierenstein and Rixon[§] obtained a hexahydroxydiphenyl, m.p. 312–317° (dried at 130°) (hexa-acetate, m.p. 164°).[‖]

A consideration of the foregoing results suggests that the products obtained by Barth and Goldschmidt in the sodium hydroxide fusion, by Harries, and by Nierenstein and Rixon are all identical, but the dipyrogallol obtained by potash fusion of ellagic acid is a different substance.

Liebermann[¶] obtained a dipyrogallol (hexa-acetate, m.p. 236°; hexamethyl ether, m.p. 126°) by reduction and demethylation of coerulignone. The synthesis of pyrogallol 1 : 3-dimethyl ether (Herzig and Pollak[††]), and the oxidation of this compound to coerulignone proves that coerulignone is 3 : 5 : 3′ : 5′ tetramethoxydiphenoquinone. Liebermann's hexahydroxydiphenyl is therefore *symm*-dipyrogallol.

Employing Ullmann's method Graebe and Suter[‡‡] converted 4- and 5-iodopyrogallol trimethyl ethers into the corresponding hexamethoxydiphenyls: 2 : 3 : 4 : 2′ : 3′ : 4′-hexamethoxy- and 3 : 4 : 5 : 3′ : 4′ : 5′-hexamethoxydiphenyl. The former melts at 123°, the latter at 126°. They repeated Barth and Goldschmidt's potash fusion of ellagic acid and methylated the product thus obtained. According to these authors the product was not homogeneous, but after exhaustive purification had m.p. 122–123° and consisted of 2 : 3 : 4 : 2′ : 3′ : 4′-hexamethoxydiphenyl. In the same way Liebermann's dipyrogallol was identified with synthetical *symm*-dipyrogallol.

In order to determine the constitution of the compound obtained by Harries, the present author has attempted to prepare it according to the method described in the literature (*loc. cit.*), but has found that the data given were insufficient and that a strict adherence to the details given resulted in complete conversion of the pyrogallol into humic acid. Systematic experiments dealing with the kinetics of the oxygen absorption led to a modification which gives reproducible and satisfactory yields.

[†] 'Ber. deuts. chem. Ges.,' vol. 12, p. 1249 (1879).

[‡] 'Mhft. Chem.,' vol. 1, p. 672 (1879).

[§] 'Liebig's Ann.,' vol. 348, p. 249 (1912).

[‖] *Cf.* also Eller, 'Liebig's Ann.,' vol. 431, p. 152 (1923).

[¶] 'Liebig's Ann.,' vol. 169, p. 241 (1873); 'Ber. deuts. chem. Ges.,' vol. 45, p. 1221 (1912).

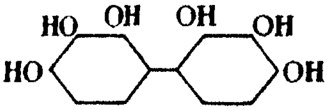
[††] 'Mhft. Chem.,' vol. 25, p. 501 (1904).

[‡‡] 'Liebig's Ann.,' vol. 340, pp. 223, 230 (1905).

The first visible stage of the oxidation is the formation of a blue-violet precipitate; this is very rapidly decolorized and yields the insoluble barium salt of the dipyrogallol. Probably the coloration is due to the formation of a quinhydrone salt analogous to those obtained by Goldschmidt and Christman† from *o*- and *p*-benzoquinone, and having the composition $C_6H_4O_2$, $C_6H_4O_2Na_2$.

The dipyrogallol yielded an acetate, m.p. 163–164°, which was easily hydrolysed by boiling dilute methyl alcoholic sulphuric acid to a pure dipyrogallol, readily oxidized in alkaline solution (hexamethyl ether, m.p. 123°, yielding a dibromo-derivative, m.p. 110–111°).

For purposes of identification the hexamethyl ether of *vic*-dipyrogallol was prepared by heating 4-iodopyrogallol trimethyl ether with copper powder. Graebe and Suter obtained this iodo-compound from the methyl ether of pyrogallolcarboxylic acid amide by converting it into the amine by the Hofmann reaction followed by diazotization and treatment with an iodide. This method is unsatisfactory, but an excellent yield of 4-iodopyrogallol trimethyl ether may be obtained by the facile action of iodine and mercuric oxide on pyrogallol trimethyl ether without the use of any solvent. The melting points of mixtures of the methyl ether of Harries' compound and its bromo-derivative with corresponding synthetic products showed no depression. It follows, therefore, that the hexahydroxydiphenyl of Harries, the first stage in the polymerization of pyrogallol in alkaline solution, is 2 : 3 : 4 : 2′ : 3′ : 4′-hexamethoxydiphenyl :



(VII)

It is difficult to form an opinion as to the nature of the substance which Barth and Goldschmidt obtained by potash fusion, and possibly the substance does not belong to the dipyrogallol series. The present author has been unable to isolate any product of the reaction other than *vic*-dipyrogallol.

It is an interesting fact that the oxidative coupling of pyrogallol is effected in different positions in solutions of varying acidity. In alkaline solution, *vic*-dipyrogallol is obtained; in neutral solution the *asymm*-dipyrogallol is formed; and in acid solution the *symm*-dimethyl ether of pyrogallol is converted into a derivative of *symm*-dipyrogallol.

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† 'Ber. deuts. chem. Ges.,' vol. 57, p. 711 (1924).

The author has made many efforts to couple pyrogallol symmetrically in strongly acid solution, but as *symm*-dipyrogallol is a very sensitive phenol, the chances of obtaining it in this way were small, and not even traces of *symm*-dipyrogallol were obtained. The anodic oxidation of pyrogallol trimethyl ether, however, furnished, along with tarry products, a considerable amount of 2 : 6-dimethoxyquinone, a result which may indicate that in strongly acid solution not only the *symm*-dimethyl ether of pyrogallol but also pyrogallol itself has a reactive 5-position. In alkaline or neutral solution the trimethyl ether of pyrogallol was found to be resistant towards anodic oxidation.

The Oxidative Coupling of Hydroxyquinol.—In alkaline solution hydroxyquinol is as labile as pyrogallol, and the formation of hexahydroxydiphenyl derivatives was observed many years ago; the literature concerning these dehydrogenation products is, however, even more confusing than that of the dipyrogallols.

The collation of the records is made difficult by the fact that different preparations melt or decompose at very varying temperatures as the result of small differences in their degree of purity.

By fusing quinol with sodium hydroxide, Barth and Schreder[†] obtained a hexahydroxydiphenyl (hexa-acetate, m.p. 169–172°) which was extremely sensitive towards oxygen.

Brezina[‡] ethylated hydroxyquinol and obtained as a by-product a hexaethoxydiphenyl; when de-ethylated it yielded a mixture of a hexahydroxydiphenyl (hexa-acetate, m.p. 169–172°) and an anhydride, tetrahydroxydiphenylene oxide.

Schuler[§] methylated hydroxyquinol with dimethyl sulphate and obtained as a by-product a hexamethoxydiphenyl, m.p. 177°. Demethylation with hydrogen iodide afforded tetrahydroxydiphenylene oxide identical with Brezina's.

Bargellini and Martegiani[||] methylated hydroxyquinol carboxylic acid and obtained asaronic acid, hydroxyquinol trimethyl ether, and a hexamethoxydiphenyl, m.p. 175–177°, as the result of decarboxylation. The last-named compound was characterized by a red colour-reaction with concentrated sulphuric acid.

[†] 'Mhft. Chem.,' vol. 5, pp. 590, 597 (1884).

[‡] 'Mhft. Chem.,' vol. 22, p. 593 (1901).

[§] 'Arch. Pharm. Berl.,' vol. 245, pp. 263, 273 (1907).

[||] 'Gazz. chem. ital.,' vol. 42 (II), p. 353 (1912).

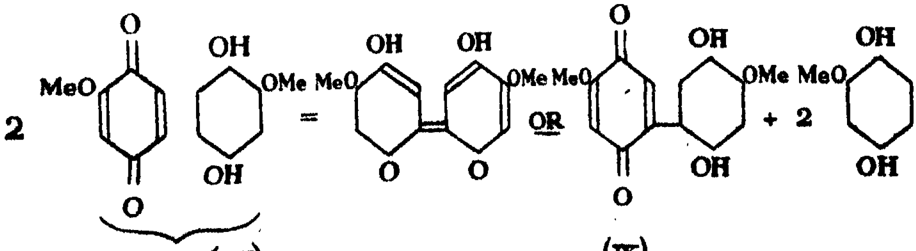
In all these experiments the dehydrogenation occurs in alkaline solution, and the products are of special interest in humic acid chemistry, as they may be ethers of the intermediates in the alkaline, oxidative polymerization of hydroxyquinol. The hydrogen in 5-position in the hydroxyquinol is very reactive, and it has therefore generally been supposed that the coupling takes place in this position.

Fabinyi and Szeki† synthesized the hexamethyl ether (m.p. 180°) of this hexahydroxydiphenyl by heating 5-bromohydroxyquinol trimethyl ether with copper.

The investigations recorded in the present paper have shown that all the above-mentioned diphenyl derivatives are identical with, or are derived from, 2 : 4 : 5 : 2′ : 4′ : 5′-hexahydroxydiphenyl.

It has not yet been possible to define conditions for the preparation of definite coupled products from hydroxyquinol itself. Hydroxyquinone is an extremely labile substance, methoxyquinone is more stable though very reactive, and toluquinone is a relatively stable quinone ; accordingly methoxyquinol was selected for a close examination of the products of its oxidative coupling.

Oxidation with ferric chloride or chromic acid does not produce methoxyquinone as stated by Will,‡ but a coupled product (VIII or IX) in quantitative yield. The same substance is rapidly formed when a trace of sulphuric acid is added to a solution of methoxyquinone in acetic acid. A further very interesting formation method is the decomposition of methoxyquinhydrone by heating at 95–100°, methoxyquinol being also produced.



(VIII) (IX)

This transformation is facilitated by traces of water ; no coupling took place when a carefully dried methoxyquinhydrone was employed, the substance dissociating into methoxyquinone and methoxyquinol.

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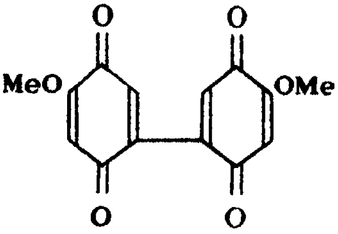
† 'Ber. deuts. chem. Ges.,' vol. 43, p. 2682 (1910).

‡ 'Ber. deuts. chem. Ges.,' vol. 20, p. 1133 (1887) ; vol. 21, p. 606 (1888).

The pronounced colour of the blue violet coupled product of methoxyquinone *and the fact that it is also obtained on partial oxidation of 4 : 4′-dimethoxydiquinol or on partial reduction of 4 : 4′-dimethoxydiquinone indicates that it is 4 : 4′-dimethoxydiquinhydrone. A characteristic property of most* quinhydrones, however, is the ease with which they undergo dissociation into their components in solution. The substance under discussion is very stable and may be crystallized from high boiling solvents, such as pyridine or nitrobenzene without the colour being discharged in the hot solution. It therefore seems more probable that the coupled compound is simply a partially oxidized 4 : 4′-dimethoxydiquinol having the structure (VIII) or (IX) representing tautomeric forms.† The vivid colour of the substance is explained on the basis of the "indigoid" formula (VIII).‡

Under certain conditions the coupled product reacts like a quinhydrone, and when warmed with acetic anhydride it yields 4 : 4′-dimethoxydiquinone (X) and the tetra-acetate of 4 : 4′-dimethoxydiquinol.



(X)

On oxidation with chromic acid the coupled product is easily converted into 4 : 4′-dimethoxydiquinone.

This normal yellow quinone, when treated with hydrogen chloride in chloroform, is rapidly converted into a colourless, very labile dichloroquinol, which could not be obtained quite pure as it dissociated into hydrogen chloride and 4 : 4′-dimethoxydiquinone on recrystallization. Merely on heating, moreover, the dry chlorophenol undergoes dissociation into these components. This remarkable reaction is of theoretical importance as an example of the reversible addition of hydrogen chloride to a quinone. The chlorophenol is instantly decomposed by alkali; its structure is not yet established, but by analogy with the results of the Thiele-acetylation of 5-methoxytoluquinone we should expect the chlorine to enter into the *ortho*-position to the methoxyl group. That position, however, is situated in the neutralized system and, hence, is not very reactive. It must not be overlooked that the two nuclei have an active conjugated system in common (XI), and it is therefore probable that the chlorophenol is 6 : 6′-dichloro-4 : 4′-dimethoxy-2 : 4 : 2′ : 4′-tetrahydroxydiphenyl (XII as acetate) (compare further the migration of dimethoxydiquinone, p. 224).

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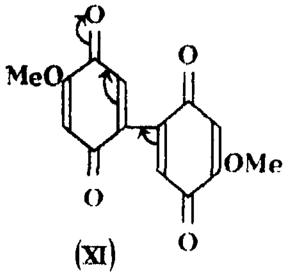
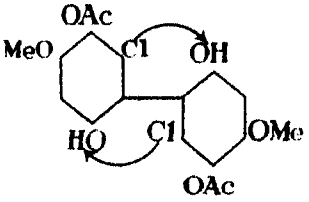
† *Cf.* Fieser, 'J. Amer. Chem. Soc.,' vol. 48, p. 2922 (1926).

‡ *Cf.* Friedländer and Schuloff, 'Mhft. Chem.,' vol. 29, pp. 387, 393 (1909); Willstätter and Schuler, 'Ber. deuts. chem. Ges.,' vol. 61, p. 363 (1928); Goldschmidt and Wessbecher, *ibid.*, vol. 61, p. 372 (1928).



(XI)



(XII)

The chlorophenol is acetylated by cold acetic anhydride containing a little concentrated sulphuric acid to a product which, according to the analytical results, is a diacetate, and which cannot be transformed into a tetra-acetate by boiling with acetic anhydride. Probably the acetate has the structure represented by the formula (XII), the chelate link between chlorine and the hydroxyl hydrogen preventing further acetylation.

When the chlorophenol is heated with acetic anhydride it is largely decomposed into hydrogen chloride and 4 : 4′-dimethoxydiquinone, but a small amount of a new substance, probably an anhydride of (XII), can be isolated from the mother liquor.

The Thiele acetylation of 4 : 4′-dimethoxydiquinone proceeds very slowly and requires several months for completion. The product obtained is a mixture of polymeric substances, a small amount of a product of rearrangement of dimethoxydiquinone (*cf.* p. 224) and a hexa-acetoxydimethoxydiphenyl; our knowledge of the last-named substance is as incomplete as that of the chlorophenol described above.

When 4 : 4′-dimethoxydiquinone or the blue-violet coupled product of methoxyquinone is reduced with zinc and acetic acid, 4 : 4′-dimethoxydiquinol is formed. This phenol absorbs oxygen very rapidly in alkaline solution and is converted into a brown amorphous humic acid. The lability of the dimethoxydiquinol, however, is not so great as that of the demethylated compound, 2 : 4 : 5 : 2′ : 4′ : 5′-hexahydroxydiphenyl, which is obtained together with its anhydride 2 : 3 : 6 : 7-tetrahydroxydiphenylene oxide, by short boiling of 4 : 4′-dimethoxydiquinol with concentrated hydrobromic acid. The former shows all the reactions recorded by Barth and Schreder (*loc. cit.*) for their hexahydroxydiphenyl, and is certainly identical with that substance. On methylation, 4 : 4′-dimethoxydiquinol easily yields the corresponding hexamethoxydiphenyl, which was found to be identical with the product obtained by the method of Fabinyi and Szeki (*loc. cit.*). It reacts violently with nitric acid, and 4 : 4′-dimethoxydiquinone crystallizes from the reaction mixture.

In order to identify the hexahydroxydiphenyl derivatives obtained from alkaline reaction mixtures with the coupled products recorded in this communication, the hexamethoxydiphenyl of Schuler (*loc. cit.*) was prepared and found to be identical with that of the present author.

These results are difficult to reconcile with the statement of Fabinyi and Szeki that their hexamethoxydiphenyl gives a green colour-reaction with concentrated sulphuric acid. This green colour-reaction is obtained only when the sulphuric acid contains some water, and when dry reagents are employed the red colour-reaction is always obtained.

It appears therefore that hydroxyquinol, as opposed to pyrogallol, couples in one and the same position (5-) whether the oxidation is carried out in acid or in alkaline solution. The same position is active when hydroxyquinol exhibits anionoid reactivity. (Bromination, nitration, condensation with aldehydes—Fabinyi and Szeki.[†]) The fact that the same position is invariably attacked in the oxidative coupling of hydroxyquinol may, perhaps, be attributed to the anionoid reactivity of hydroxyquinol and the kationoid reactivity of its dehydrogenation products being exhibited at a single carbon atom.

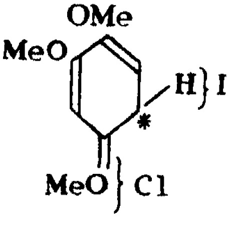
The Oxidative Coupling of Hydroxyquinol Trimethyl Ether.—Nietzki, by treating toluquinol dimethyl ether with chromic acid, obtained an (indigoid) quinone of the ditolyl type, the structure of which has been elucidated by the present author (pp. 206, 219).

When hydroxyquinol trimethyl ether was treated in a similar manner, but under milder conditions, most of the trimethyl ether was almost instantly converted into 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl. A small amount of the indigoid quinone (IX) could be isolated as a by-product.

It is remarkable that a phenol ether so easily undergoes a dehydrogenation, and the mechanism in this reaction is, of course, different from that of the ordinary phenol dehydrogenations. The reaction can be effected by almost any oxidizing agent (anodic oxidation, ferric chloride, etc.), but it occurs in acid solutions only.

[†] 'Ber. deuts. chem. Ges.,' vol. 43, p. 2682 (1910).

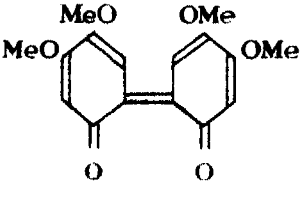
The following very unexpected reaction is of special interest in arriving at an explanation of the coupling process. When treated with iodine chloride in acetic acid solution, hydroxyquinol trimethyl ether yields hydrogen chloride and 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl in the form of a labile iodine addition compound. The 5-iodohydroxyquinol trimethyl ether which might be expected is not formed. As the coupling of the trimethyl ether of hydroxyquinol only takes place in acid solution we may assume that oxonium salt formation initiates the reaction, for example in the case of iodine chloride, the formation of (XIII) or a *p*-quinonoid alternative.



(XIII)

This complex then loses hydrogen chloride and iodine, and the two remaining radicals polymerize to yield hexamethoxydiphenyl.

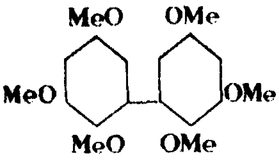
It should be noted that the oxonium salts are much less stable than ammonium salts, for example, and it is therefore not unnatural that a similar chromic acid complex easily loses the methyl group (as methyl alcohol or formaldehyde) yielding the indigoid quinone (XIV).



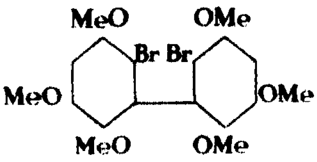
(XIV)

This blue-violet quinone resembles the coupled product of methoxyquinone; it is oxidized by nitric acid to 4 : 4′-dimethoxydiquinone, and this reaction excludes the theoretically possible diphenoquinone structure. Another possibility is that one nucleus is *p*-quinonoid and the other benzenoid, but this is excluded by the close analogies of the quinone with the indigoid ditolyl-quinone of Nietzki, in which the *p*-quinonoid structure has been definitely disproved.

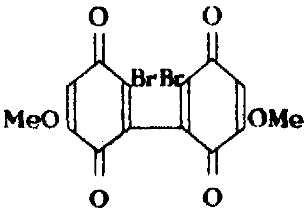
Derivatives of 2 : 3 : 5 : 2′ : 3′ : 5′-*Hexahydroxydiphenyl.*—In view of the foregoing it was of interest to study the reactivity of other bis-hydroxyhydroquinones, and more especially that of 2 : 3 : 5 : 2′ : 3′ : 5′-hexahydroxydiphenyl. The 3 : 3′-dimethyl ether of this phenol is easily obtained by the application of the Dakin reaction† to dehydrodivanillin ; it is a very labile substance easily oxidized to amorphous substances in alkaline solution. It was not possible to oxidize it to a diquinone with chromic acid or with ferric chloride, since polymerization immediately occurred. On acetylation, the corresponding tetra-acetate was obtained, and this could easily be brominated to a dibromo-derivative. On methylation the phenol yielded 2 : 3 : 5 : 2′ : 3′ : 5′-hexamethoxydiphenyl (XV) which undergoes bromination (XVI) and nitration with the same ease as the trimethyl ether of hydroxyquinol. This indicates clearly that the characteristic reactivity of the 5-position of hydroxyquinol is preserved in spite of the diphenyl linkage. The derivatives mentioned above must consequently be 6 : 6′-substituted.



(XV)



(XVI)



(XVII)

When 2 : 3 : 5 : 2′ : 3′ : 5′-hexamethoxy-6 : 6′-dibromodiphenyl is treated with strong nitric acid a stable diquinone (XVII) is obtained.

The Coupling of Toluquinol : Bis-derivatives of Toluquinol.—In its general reactivity toluquinol is very closely related to hydroxy and methoxyquinol. The carbon atom in position-5 is highly anionoid, as is that of the two latter phenols ; the degree of reactivity of toluquinol, however, is very much lower. The interest of a study of the coupling reactions of toluquinol and of toluquinone is not the potential occurrence of " toluquinol humic acid " in Nature, but it provides us with valuable analogies of the reactions studied in the hydroxyquinol series. Methoxyquinone, because of its great reactivity and the homogeneity of the products of reaction, is of importance for the theoretical understanding of coupling reactions of the quinones. With toluquinone, however, we are able to study in greater detail several interesting compounds corresponding to those which were obtained only with a great difficulty, or in a poor yield, during the investigations in the hydroxyquinol series. It has also been possible to isolate a termolecular product of the polymerization of toluquinone ; this provides us with a very welcome *experimental* indication as to the nature of the further coupling of quinones to the complex amorphous products which are related to humic acid.

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† 'J. Amer. Chem. Soc.,' vol. 42, pp. 479, 496 (1909).

In this section only substances of the ditolyl type will be considered ; the termolecular compound is discussed in IV (p. 229).

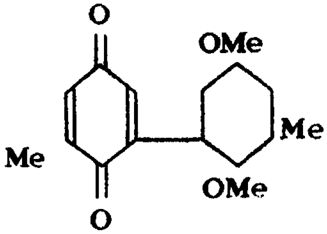
Spica[†] found that toluquinone when treated with 50% sulphuric acid is transformed into a brown-black "toluquinone polymeride." He showed, however, that the crude product, which had only been dissolved in acetic acid and precipitated with water, was not a pure compound, but a mixture of a large amount of a material insoluble in chloroform, and a small amount of a second violet substance, which was slightly soluble in chloroform. The latter product corresponds in composition with that of a true polymeride of toluquinone $(C_7H_6O_2)_n$. The author has repeated the experiment in detail and has no doubt that Spica's "polymeride" is the equivalent in the toluquinone series of the coupled product of methoxyquinone, which has been described above (p. 199). The yield of this substance is not good, however, partly because the conversion of toluquinone into the coupled product proceeds slowly, and partly because the coupled product itself slowly reacts with toluquinone or toluquinol to yield a tritolyl derivative. This was the chief product (insoluble in chloroform) in Spica's experiment, but he did not investigate it further. As regards the structure of the dimolecular coupled product of toluquinone, the arguments used above against the quinhydrone structure hold good for this product also.

As has already been mentioned, Nietzki,[‡] by oxidizing toluhydroquinone dimethyl ether with chromic acid obtained a quinonoid product containing two methoxy groups. Noelting and Werner[§] prepared the corresponding ethyl derivative and attempted unsuccessfully to prove the indigoid structure of this and Nietzki's substance. Nietzki (*loc. cit.*) methylated toluquinol partially and obtained a mixture of the crude 1-methyl and the 4-methyl ethers of toluquinol. Bamberger[†] obtained the pure 1-methyl ether, and stated that with ferric chloride it yielded a brownish-violet crystalline substance, but he did not identify this with Nietzki's quinone. These statements make it very probable that Nietzki's quinone is an indigoid quinone. Nietzki and Bernard,[‡] however, oxidized this quinone with nitric acid and obtained a ditoluquinone identical with that obtained by Brunner[§] as a product of oxidation of toluquinol in sulphuric acid solution with manganese dioxide. Disregarding Nietzki's experiments on the oxidation of the impure monomethyl ether of toluquinol, Nietzki and Bernard concluded that the violet quinone is *p*-quinonoid and that the two methoxy-groups belong to the same nucleus. They accepted the arbitrary assumption by Brunner that the diphenyl linkage is produced in *m*-position to the methyl groups, and assigned the following structure to the oxidation product of toluquinol dimethyl ether:

[†] 'Gazz. chim. ital.,' vol. 12, p. 225 (1882).

[‡] 'Liebig's Ann.,' vol. 215, p. 166 (1882).

[§] 'Ber. deuts. chem. Ges.,' vol. 23, p. 3247 (1890).



(XVIII)

As indigoid quinones are of great theoretical importance and have been little studied, the author decided to prove or disprove conclusively the formula of Nietzki and Bernard.

Reduction of the ditoluquinone of Brunner and of Nietzki and Bernard yields ditoluquinol, which is converted by methylation into ditoluquinol tetramethyl ether. The same substance has now been obtained by applying the Ullmann reaction to 5-iodotoluquinol dimethyl ether. It follows that the methyl groups are situated in the para-position to the diphenyl linkage and, indeed, the substance exhibits colour reactions similar to those of 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl.

If Nietzki's oxidation product of toluquinol dimethyl ether is a *p*-quinone, it follows that reduction to the quinol and ethylation should give the same dimethoxy-diethoxy-ditolyl as is obtained by reduction and methylation of

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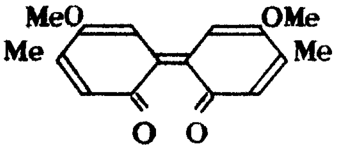
[†] 'Liebig's Ann.,' vol. 390, p. 176 (1912).

[‡] 'Ber. deuts. chem. Ges.,' vol. 31, p. 1337 (1898).

[§] 'Mhft. Chem.,' vol. 10, p. 181 (1889).

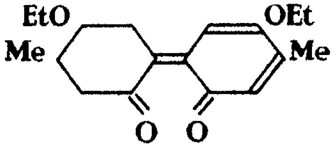
Noelting and Werner's oxidation product of toluquinol diethyl ether. If, however, the two preparations are not identical, then the indigoid formula is correct. In actual fact, the mixed ethers were found to be different.

"*Nietzki's quinone.*



(XIX)

Noelting and Werner's quinone."



(XX)

Dibenzoquinone.—It has not yet been possible to convert *p*-benzoquinone into a diphenyl derivative by means of sulphuric acid. The condensation proceeds further with the formation of high-molecular amorphous compounds, and only a small amount of a termolecular product of polymerization could be isolated in a crystalline state (*cf.* Part III).

Barth and Schreder† obtained diquinol as a product of the alkaline fusion of quinol, and oxidized it to diquinone. This quinone has also been synthesized by Hale and Robertson‡ and by Borsche and Scholten§ from *o* : *o*′-diphenol; the author has found that the method of Borsche and Scholten is the best.

Diquinone is very stable, and the Thiele-acetylation requires 24 hours; addition of hydrogen chloride is facile. As the diphenyl linkage has only a weak orientating power, no pure substances could be obtained from these reactions, the products being non-crystallizable syrups, obviously consisting of mixtures of isomerides. The product of the addition of hydrogen chloride was instantly decomposed by alkali, yielding a green solution. It is an interesting fact that whereas diquinone is decomposed by alkali to a brown solution, *p*-benzoquinone yields a green solution.

Some compounds are described (p. 221) which were obtained during unsuccessful attempts to synthesize diquinone from other starting materials than *o* : *o*′-diphenol.

EXPERIMENTAL.

2 : 3 : 4 : 2′ : 3′ : 4′-*Hexadydroxydiphenyl* (*Harries' Dipyrogallol*).—An aqueous solution (150 c.c.) of pyrogallol (10 gm.) was quickly added to a baryta solution (50–60 gm. in 1670 c.c.) contained in a bottle of 3000 c.c.

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† 'Mhft. Chem.,' vol. 5, pp. 590, 600 (1884).

‡ 'J. Amer. Chem. Soc.,' vol. 39, p. 692 (1908).

§ 'Ber. deuts. chem. Ges.,' vol. 50, p. 596 (1917).

capacity, which was stoppered and shaken vigorously for 5 minutes. The end-point was indicated by the non-appearance of a blue-violet tint on the surface of the liquid when the agitation was interrupted. The mixture was allowed to stand for about 15 minutes (grey brown precipitate), and light petroleum was then added. The precipitate was collected, air being excluded and, while still covered with petroleum, it was washed with air-free water. It was then decomposed with hydrochloric acid (14%) and the precipitated hexahydroxydiphenyl (yield 50–60%) was collected, washed with water, and recrystallized from water containing acetic acid or sulphurous acid. After being dried in a vacuum at 130° it darkens at about 280° and melts at 310–320° (decomp.). During the oxidation part of the pyrogallol is further oxidized to pyrogallol-humic acid, and the corresponding amount of pyrogallol is found unchanged in the baryta solution.

Oxidation of Pyrogallol in Sodium Hydroxide Solution.—Pyrogallol (10 gm.) was oxidized as described above, but sodium hydroxide (10 gm.) was used instead of baryta; no blue-violet coloration was observed. After shaking for 10 minutes, oxygen absorption was complete, and barium chloride (50 gm. in water) was introduced. A small amount of a light brown precipitate was formed, and this, when treated with hydrochloric acid, yielded only pyrogallol-humic acid, but no dipyrogallol. It is obvious that the baryta method owes its success to the insolubility of the barium salt of dipyrogallol.

Hexa-acetate.—Crude hexahydroxydiphenyl was refluxed with excess of acetic anhydride and sodium acetate (or pyridine) for half an hour. The acetate crystallized from acetic acid or alcohol in needles, m.p. 163–164°. Pure hexahydroxydiphenyl was obtained when the pure hexa-acetate was refluxed with not too large a volume of 2% methyl alcoholic sulphuric acid for 30 minutes, the sulphuric acid then neutralized with barium carbonate, and the filtrate concentrated in vacuum.

Hexamethyl Ether.—The same crude dipyrogallol was methylated by the method of Chapman, Perkin and Robinson.† The product crystallized from acetic acid in white needles, m.p. 123° (found: MeO, 55·5. $C_{12}H_4(OMe)_6$ requires MeO, 55·7%). Nitric acid attacks it easily, giving uncrystallizable products.

Dibromohexamethyl Ether.—Dipyrogallol hexamethyl ether was dissolved in chloroform and treated with a dilute solution of bromine in chloroform until the brown colour persisted. The bromo-compound crystallized from dilute acetic acid in pearly shining plates, m.p. 110–111° (found: Br. 32·3. $C_{12}H_2Br_2(OMe)_6$ requires Br. 32·5%).

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† 'J. Chem. Soc.,' p. 3028 (1927).

4-Iodopyrogallol Trimethyl Ether.—Pyrogallol trimethyl ether (13·4 gm.) was melted and stirred continuously while iodine (24·4 gm.) and mercuric oxide (10–12 gm.) were added in small portions at a time. The temperature was maintained at about 80°, and the iodine was consumed rapidly. The reaction product was extracted with a mixture of ether and petroleum ether (1 : 1), or with benzene, and the solution was shaken with aqueous sodium iodide. On slow evaporation, large rhombic crystals were formed. The substance was purified by distillation (yield, 70–72% of colourless crystals, m.p. 40–42°).

2 : 3 : 4 : 2′ : 3′ : 4′-*Hexamethoxydiphenyl.*—4-Iodopyrogallol trimethyl ether was heated with copper powder as described by Graebe and Suter (*loc. cit.*); the product, m.p. 123° after recrystallization from acetic acid, yielded a bromo-derivative, m.p. 110–111°. Mixed melting points with corresponding substances obtained from Harries' compound showed no depression.

Oxidation of Pyrogallol in Acid Solution.—As these experiments did not furnish any positive results, only one of them will be described briefly, in order to indicate the method generally adopted.

A solution of pyrogallol (10·6 gm.) in N sulphuric acid was electrolysed for 3 hours using a current of 0·2 amp. The lead anode, coated with lead peroxide, had a surface of 45 cm.^{2}. Even at the beginning of the electrolysis the solution turned brown, and the colour gradually deepened and ultimately became black. The electrolyte was extracted three times with 25 c.c. of ether to remove most of the unchanged pyrogallol (*symm*-dipyrogallol is very sparingly soluble in ether) and was then extracted exhaustively with ether. The latter extract was dried and distilled and the residual solid acetylated. The acetate was fractionally crystallized, and found to consist exclusively of pyrogallol acetate and some brown amorphous impurities. The conditions were varied widely, *e.g.*, concentration of the acid, time, current strength and anode material (oxidized or non-oxidized lead surface, platinum), but no *symm*-dipyrogallol could be detected. In neutral solution purpurogallin is formed in good yield.†

Anodic Oxidation of Pyrogallol Trimethyl Ether to 2 : 6-*Dimethoxyquinone.*—In this series of experiments the oxidation was carried out under widely varied conditions.

A solution of pyrogallol trimethyl ether (8·4 gm.) in acetone (50 c.c.) and 2 N sulphuric acid (50 c.c.) was electrolysed during 9 hours, employing a current of 1 amp. and no stirring. The anode surface (lead peroxide) was 70 cm.^{2}. The quinone, which was deposited on the anode, was collected at hourly intervals. The acetone was evaporated in the air, water was added, and the oil collected, diluted with some methyl alcohol and the precipitated 2 : 6-dimethoxyquinone was collected (yield, 2–2·5 gm.). The oily matter was extracted with alkali, and the insoluble portion which could not be induced to crystallize was distilled in a vacuum. Most of the material charred and the small amount of distillate could not be crystallized either as such or as a bromo-derivative. The 2 : 6-dimethoxydiquinone was identified by its melting point (255°) and by conversion into 2 : 6-dimethoxyquinol diacetate by reductive acetylation. This acetate, crystallized from acetic acid, had m.p. 133°. Hofmann† and Hesse‡ record the m.p. as 128° after recrystallization from water, and the author has observed this melting point when the preparation, m.p. 133°, was recrystallized once from water.

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† Perkin and Perkin, 'J. Chem. Soc.,' vol. 85, p. 244 (1904).

In another experiment the oxidation of the pyrogallol trimethyl ether was carried out as above, but a 2 N solution of potassium carbonate was employed instead of sulphuric acid. In this experiment two layers were formed and vigorous stirring was needed. At the end of the electrolysis the trimethyl ether was recovered almost quantitatively (97%).

Thermal Decomposition of Methoxyquinhydrone.

Methoxyquinone (1 mol.) and methoxyquinol (1 mol.) were dissolved in 50 times their combined weights of hot, dry benzene. The faintly greenish solution, on evaporation in a current of air, deposited the methoxyquinhydrone in brownish-violet needles, sintering at about 90° (slowly heated); heated rapidly, m.p. 97° (colour change from brown-violet to blue-black).

Methoxyquinhydrone (2 gm.) was heated at 95–100° for about 15 minutes, and the black crystalline mass was extracted with ether. The residue (0·9 gm.) was identified with the coupled product described below by comparison of the decomposition-points and behaviour on oxidation and reductive acetylation. The ether-soluble fraction was methoxyquinol.

The same experiment was carried out with methoxyquinone which had been dried over sodium hydroxide and phosphoric anhydride for 14 days. After being heated for about 5 or 10 minutes the substance had acquired a greenish metallic lustre and was washed with ether which dissolved methoxyquinol, and pure methoxyquinone remained undissolved.

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† 'Ber. deuts. chem. Ges.,' vol. 11, p. 333 (1878).

‡ 'Liebig's Ann.,' vol. 276, p. 332 (1893).

The Coupled Product of Methoxyquinone.—A solution of hydrogen peroxide (25 c.c. of 30%) in water (200 c.c.) was added to vanillin (30 gm.) dissolved in aqueous sodium hydroxide (200 c.c. of 4%). After 15 minutes the brown solution was acidified by concentrated hydrochloric acid (50 c.c.), heated to 30–40° (not higher) and a slight excess of concentrated aqueous ferric chloride was gradually added. The liquid immediately became dark brown, and the blue-violet coupled product soon separated. After standing for half an hour the thick reaction mixture was filtered, and the precipitate (18–19 gm.) thoroughly washed with water, alcohol, and ether. The same product was obtained when a little sulphuric acid diluted with acetic acid was added to a solution of methoxyquinone in almost any solvent, *e.g.*, acetic acid. The solution instantly turned brown and after a few seconds crystallization took place (yield 98%). The coupled product was very sparingly soluble in low-boiling organic solvents, fairly readily soluble in hot *n*-butyl alcohol and pentachloroethane forming blue-violet solutions and was easily soluble in hot pyridine with a red-violet colour. It gave a green solution in aqueous alkalis and was decomposed by this treatment. It was very resistant towards sulphurous acid, but was reduced to the diquinol by phenylhydrazine. For analysis the substance was recrystallized several times from boiling pyridine and the crystals (soft needles) washed with dilute acetic acid and then with alcohol and ether. It began to sinter at 210° and decomposed rapidly at 230° (found: C, 61·0; H, 4·7. $C_{14}H_{12}O_6$ requires C, 60·9; H, 4·4%).

4 : 4′-*Dimethoxydiquinone.*—A very dilute solution of chromic acid was added to the vigorously stirred suspension of the coupled product from the previous experiment. The yellow, sparingly soluble diquinone was collected (yield, 18–19 gm.), washed with water, alcohol, and ether, and crystallized from acetic acid or better from acetic anhydride, in yellow needles which decomposed at 212–214° with the formation of a red product of rearrangement (*cf.* p. 224). It is advisable to carry out the recrystallizations in absence of light† in order to avoid lowering the yield (found: C, 61·4; H, 3·3; MeO, 22·8. $C_{12}H_4O_4(OMe)_2$ requires C, 61·3; H, 3·7; MeO, 22·6%). 4 : 4′-dimethoxydiquinone is decomposed by phenylhydrazine with the evolution of nitrogen and by alkali to a green solution which turned brown in the air.

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† It is an interesting fact that most diquinones when subjected to the action of light yield red substances or some modifications. (*Cf.* Chattaway, 'J. Chem. Soc.,' vol. 67, p. 662 (1895).) Dimethoxyquinone is rapidly converted to a red product by the action of direct sunlight when spread in a thin layer. Diquinone and ditoluquinone undergo a similar change, but more slowly.

2(?) : 3 : 6 : 2′(?) : 3′ : 6′-*Hexa-acetoxy*-4 : 4′-*dimethoxydiphenyl.*—A suspension of 4 : 4′-dimethoxydiquinone (10 gm.) in acetic anhydride (200 c.c.) and sulphuric acid (5 c.c.) was kept at the room temperature for a month and shaken frequently. The filtrate from unchanged diquinone (5·5 gm.) was decomposed with water, and the red-brown precipitate was washed with alcohol which dissolved a considerable quantity of amorphous substances and nearly all the red colouring matter (*cf.* p. 224). The crude acetate was crystallized from acetic acid in colourless needles, m.p. 200° (found: C, 55·7; H, 4·6. $C_{26}H_{26}O_{14}$ requires C, 55·5; H, 4·6%). The substance was easily hydrolysed by alcoholic sodium hydroxide. The phenol thus obtained absorbed oxygen yielding a permanganate coloured solution which on acidification turned yellow.

Attempts to demethylate this compound with hydrogen iodide in order to compare the parent phenol with the octahydroxydiphenylene of Perkin† have not yet been successful. Along with amorphous products, a very minute quantity of a colourless crystalline substance was obtained and isolated by evaporating the reaction-mixture almost to dryness in a vacuum. The crystals instantly turned dark blue when treated with distilled water. With pyridine-acetic anhydride, an acetate, m.p. 264–266°, was obtained, and this did not show any colour reaction with sulphuric acid. Owing to the small amount available complete purification could not be effected, but the analytical data lay between those required for an octa-acetoxydiphenyl and those for a hexa-acetoxydiphenylene oxide.

Addition of Hydrogen Chloride to 4 : 4′-*Dimethoxydiquinone.*—Hydrogen chloride was passed through a fine suspension of 4 : 4′-dimethoxydiquinone in chloroform, to which a little acetic acid had been added, until the diquinone was completely converted into a brownish mass of prismatic crystals. The chloroform was evaporated in a vacuum at the ordinary temperature over paraffin and sodium hydroxide and the chlorophenol could not be purified since it decomposed into hydrogen chloride and dimethoxydiquinone on recrystallization from acetic acid, alcohol, etc. It was, therefore, merely washed with methyl alcohol and ether which dissolved the brownish impurities and yielded a colourless preparation. The chlorophenol had no definite melting point as it yielded dimethoxyquinone on heating (found: Cl, 18·7. $C_{14}H_{12}O_6Cl_2$ requires Cl, 20·5%). Though the substance was not pure the analysis proved that two molecules of hydrogen chloride reacted with one molecule of the diquinone. The chlorophenol dissolved in alkali with a green colour similar to that given by 4 : 4′-dimethoxydiquinone, and when the organic matter had been precipitated with baryta and removed by filtration, the filtrate contained chlorides.

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† 'J. Chem. Soc.,' vol. 99, p. 1447 (1911).

A solution of the chlorophenol in acetic anhydride containing 1% of sulphuric acid was kept at the room temperature for 12 hours. The filtrate from dimethoxydiquinone was decomposed with water, and the solid recrystallized from acetic acid or acetic anhydride to constant m.p. 232°; colourless, prismatic needles, sparingly soluble in most organic solvents except acetone (found: C, 50·0; H, 3·9; MeO, 14·0; Cl, 16·6. $C_{18}H_{16}O_8Cl_2$ requires C, 50·1; H, 3·7; MeO, 14·4; Cl, 16·5%). According to these analyses the substance is a diacetate; it is unchanged by long boiling with acetic anhydride, but is immediately decomposed by warm aqueous sodium hydroxide; with hot methyl alcoholic sulphuric acid it yields 4 : 4′-dimethoxydiquinone and hydrogen chloride.

The Anhydride (?).—The chlorophenol from dimethoxydiquinone (10 gm.) was boiled for 10 minutes with acetic anhydride (50 c.c.) in a current of air. When cold, the solution was filtered from dimethoxydiquinone (7·5 gm.), and the mother liquor decomposed with water. Red crystals (2·5 gm.) were precipitated, but became nearly colourless when washed with acetic acid (the red substance was the acetate of a product of rearrangement of dimethoxydiquinone (*cf.* p. 224). The solid was recrystallized from acetic anhydride in colourless prisms, m.p. 253° (found: C, 52·9; H, 3·5; MeO, 15·1; Cl, 16·8. $C_{18}H_{14}O_7Cl_2$ requires C, 52·3; H, 3·4; MeO, 15·0; Cl, 17·2%), sparingly soluble in most organic solvents with the exception of acetone. The substance was resistant towards hydrolysis and gave a blue solution in sulphuric acid.

4 : 4′-*Dimethoxydiquinol.*—On passing sulphur dioxide into a suspension of 4 : 4′-dimethoxydiquinone in boiling water the quinone was slowly reduced to the coupled product of methoxyquinone (above).

Hydriodic acid and phenylhydrazine easily reduced the diquinone to 4 : 4′-dimethoxydiquinol, which crystallized from dilute alcohol containing some sulphuric acid as a colourless crystal powder, m.p. 210° (decomp.) (found: C, 60·0; H, 5·1; MeO, 22·3. $C_{12}H_8O_4(OMe)_2$ requires C, 60·4; H, 5·0; MeO, 22·3%). When moist, the phenol was rapidly oxidized in the air to the blue-violet coupled product, but in the dry state it was quite stable. Hot dilute nitric acid converted the phenol into 4 : 4′-dimethoxydiquinone by way of the blue-violet substance, and in alkaline solution it was very sensitive towards oxygen and yielded a brown humic acid.

4 : 4′-*Dimethoxydiquinol Tetra-acetate.*—The diquinol was heated on the steam-bath for 15 minutes with a mixture of pyridine and acetic anhydride and the acetate was crystallized from acetic acid in white needles, m.p. 186–187° (found: MeO, 14·0. $C_{12}H_4(AcO)_4(MeO)_2$ requires MeO, 14·0%). It was easily hydrolysed both by acids and alkali. The same product was obtained on reductive acetylation (zinc, acetic acid, and acetic anhydride) of 4 : 4′-dimethoxydiquinone or the coupled product from methoxyquinone.

2 : 4 : 5 : 2′ : 4′ : 5′-*Hexamethoxydiphenyl.*—The acetyl derivative was hydrolysed by refluxing with dilute methyl alcoholic sulphuric acid (30–60 minutes). Most of the methyl acetate was distilled, and the acid just neutralized with a strong solution of sodium hydroxide with exclusion of air. Twice the theoretical amount of dimethyl sulphate was introduced, and a slight excess of a 40% solution of sodium hydroxide was added drop by drop to the vigorously stirred mixture, any considerable rise in the temperature being carefully avoided and air being excluded. The hexamethyl ether separated as a fine crystalline powder (yield, 85–95%), and crystallized from acetic acid in snow-white needles, m.p. 177–179° (found: MeO, 55·4. $C_{12}H_4(MeO)_6$ requires MeO, 55·7%). It was easily soluble in cold ethyl acetate, chloroform, acetone, and pyridine, and was readily soluble in most other solvents on heating. It reacted vigorously with nitric acid yielding 4 : 4′-dimethoxydiquinone. The action of bromine vapour produced a green coloration, and the solution in sulphuric acid was deep blood-red in colour, becoming green and then yellow on dilution with water. This hexamethoxydiphenyl was compared directly with the preparations obtained by repeating the experiments of Schüler and of Fabinyi and Szeki (*loc. cit.*), and all the preparations were found to be identical.

2 : 4 : 5 : 2′ : 4′ : 5′-*Hexa-acetoxydiphenyl and* 2 : 3 : 6 : 7-*Tetra-acetoxydiphenylene Oxide.*—The tetra-acetate of 4 : 4′-dimethoxydiquinol (5 gm.) was refluxed with hydrobromic acid (50 c.c.; d. 1·5) during 15 minutes; the reaction product partly crystallized. The solid was isolated and at once acetylated with a mixture of acetic anhydride and pyridine. The crude product separated from much hot acetic acid as needles consisting of tetra-acetoxydiphenylene oxide, m.p. 262° after recrystallization from acetic acid or acetic anhydride (found: C, 59·8; H, 4·1. Calc. for $C_{20}H_{16}O_9$: C, 60·0; H, 4·0%). Apart from the higher melting point now recorded the substance possessed all the properties described by previous authors (*loc. cit.*).

Water was added to the mother liquor from the tetra-acetoxydiphenylene oxide, and the precipitate was crystallized from alcohol or acetic acid and then melted at 172–174°. This methoxyl-free substance consisted of 2 : 4 : 5 : 2′ : 4′ : 5′-hexa-acetoxydiphenyl. The 2 : 4 : 5 : 2′ : 4′ : 5′-hexahydroxydiphenyl obtained by cautious hydrolysis with dilute methyl alcoholic sulphuric acid in an atmosphere of hydrogen, dilution with water containing sulphurous acid and extraction with ether, possessed all the properties recorded by Brezina and by Barth and Schreder (*loc. cit.*).

Action of Iodine Chloride or of Iodine and Mercuric Oxide on Hydroxyquinol Trimethyl Ether.—When equimolecular amounts of iodine chloride and hydroxyquinol trimethyl ether, each dissolved in 5 volumes of glacial acetic acid, were mixed, a black precipitate was immediately formed and hydrogen chloride was liberated. Warm water decomposed the black precipitate into iodine and 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl (yield, quantitative).

Similarly, mercuric oxide (0·5 mol.) was slowly added to a stirred mixture of iodine (1 mol.) and hydroxyquinol trimethyl ether (1 mol.), when the mass gradually became solid and acquired a black colour owing to the formation of the addition compound of iodine and 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl.

Action of Chromic Acid on Hydroxyquinol Trimethyl Ether.—Hydroxyquinol trimethyl ether was shaken with an excess of a chromic acid solution (1–4%). The dark jelly was collected, washed with water, dried and dissolved in the minimum of hot acetic acid. Zinc dust was then added and the colourless solution was filtered into one of sodium hydroxide. A large amount of 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl was precipitated and removed by filtration. The alkaline solution was immediately acidified by acetic acid and mixed with ferric chloride solution. From dilute solutions prepared in this way, the indigoid quinone crystallized slowly in the form of beautiful, brown-violet, lustrous needles, but more concentrated solutions afforded a blue-black crystalline powder; the yield was unsatisfactory. Recrystallized from a mixture of 9 volumes of light petroleum (b.p. 100–120°) and one volume of acetic acid the quinone had m.p. 185–187° (found: C, 62·9; H, 5·4; MeO, 40·3. $C_{16}H_{16}O_6$ requires C, 63·2; H, 5·3; MeO, 40·8%). It was insoluble in water, sparingly soluble in ether and dissolved easily in acetone, chloroform, and pyridine to permanganate coloured solutions. It was immediately converted into 4 : 4′-dimethoxydiquinone by concentrated nitric acid and it was resistant towards sulphurous acid.

This quinone was obtained in better yield by anodic oxidation of hydroxyquinol trimethyl ether. The conditions were varied widely and only a few typical experiments need be mentioned here.

Anodic Oxidation of Hydroxyquinol Trimethyl Ether in Strongly Acid Solution.—A mixture of hydroxyquinol trimethyl ether (0·025 mol.), acetone (25 c.c.), and 2 N sulphuric acid (25 c.c.) was electrolysed for 6 hours at 0·5 amp. The anode was a lead sheet (surface, 35 cm.^{2}) which had previously been covered electrolytically with a layer of lead peroxide. The liquid rapidly became red and after the electrolysis it was poured into a crystallizing dish and kept until the acetone had evaporated, and a mixture of the indigoid quinone (yield, 10–15%) and 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl had separated.

Anodic Oxidation of Hydroxyquinol Trimethyl Ether in Weakly Acid Solution.—A mixture of hydroxyquinol trimethyl ether (0·025 mol.), acetone (25 c.c.), sodium sulphate (10 gm.), water (75 c.c.), and sulphuric acid (2 N, 5 c.c.) was electrolysed during 8 hours, employing a current of 0·2 amp. and good mechanical stirring. The anode was of pure lead and had a surface of 70 cm.^{2}. On evaporation of the acetone, a black, sticky mass was obtained and only traces of the indigoid quinone could be isolated from this material, which consisted largely of 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl. The yield of the pure hexamethyl ether was 85%.

Anodic Oxidation of Hydroxyquinol Trimethyl Ether in Weakly Alkaline Solution.—One experiment was carried out in the same manner as the oxidation in weakly acid solution. Sodium carbonate was employed instead of sodium sulphate, and no sulphuric acid was added. Under these conditions the hydroxyquinol trimethyl ether was not attacked and was recovered almost quantitatively.

Dehydrodivanillin.—The dehydrodivanillin was prepared according to the method of Elbs and Lerch,† but the following method of purification was found to be an improvement. Dehydrodivanillin (10 gm.) was boiled for 10 minutes with pyridine (50–75 c.c.) and an equal volume of boiling acetic acid was then added. After cooling to about 50°, the solid was collected, washed with acetone and ether and the operation was repeated.

3 : 3′-*Dimethoxydiquinol* (*Tetra-acetate*).—The theoretical quantity (*cf.* Dakin, *loc. cit.*) of 3% hydrogen peroxide was added to an aqueous solution of dehydrodivanillin (60 gm.) and sodium hydroxide (16 gm.). After 5 minutes, dilute sulphuric acid was added to the deep brownish-black reaction mixture until it was weakly acid; the precipitate was collected, digested with acetone, leaving dehydrodivanillin (10 gm.) undissolved. The acetone solution was dried and evaporated to dryness; the filtrate from the reaction mixture was exhausted with ether and the combined residues from the acetone and ether extractions

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† 'J. prakt. Chem.,' vol. 93, p. 3 (1916).

were acetylated with acetic anhydride and pyridine. The product was repeatedly extracted with small volumes of methyl alcohol, which dissolved much amorphous, dark coloured material leaving moderately pure crystalline 3 : 3′-dimethoxydiquinol tetra-acetate (25–30 gm.). After crystallization from acetic acid it formed small colourless prisms and melted at 176–178° (found: MeO, 13·7. $C_{20}H_{16}O_8(MeO)_2$ requires MeO, 14·0%).

Reductive acetylation of the brown material in the methyl alcoholic solution afforded a light yellow powder which developed a blue coloration with mineral acids.

The 3 : 3′-dimethoxydiquinol tetra-acetate was very easily hydrolysed on boiling with dilute methyl alcoholic sulphuric acid, but it is difficult to avoid a slight decomposition to amorphous substances which give a blue colour reaction with acids under these conditions. The phenol was obtained by dilution with water and extraction with ether. It was difficult to prepare it in a pure state as it polymerized with ease. It was not possible to oxidize it to a diquinone with chromic acid or with ferric chloride and in both reactions only amorphous products were obtained. In alkaline solution the phenol absorbed oxygen rapidly and was converted into a brown amorphous "humic acid."

Attempts were made to demethylate the phenol with hydriodic acid or hydrobromic acid, but only brown or blue-black amorphous products were obtained which on reductive acetylation yielded an almost colourless substance which closely resembled the methyl-alcohol-soluble by-product.

6 : 6′-*Dibromo*-3 : 3′-*Dimethoxydiquinol Tetra-acetate.*—A dilute solution of bromine in acetic acid was slowly added to pure 3 : 3′-dimethoxydiquinol tetra-acetate dissolved in a large amount of the same solvent. The bromine was rapidly absorbed, and the mixture was poured into water, the precipitate collected, washed with methyl alcohol, and recrystallized from acetic acid. It formed white needles, m.p. 207–208° (found: MeO, 9·9; Br, 25·6. $C_{20}H_{14}O_8(MeO)_2Br_2$ requires MeO, 10·3; Br, 26·5%).

2 : 3 : 5 : 2′ : 3′ : 5′-*Hexamethoxydiphenyl.*—3 : 3′-Dimethoxydiquinol tetra-acetate (5 gm.) was hydrolysed with 2% methyl alcoholic sulphuric acid, and the phenol was then methylated using twice the theoretical amount of dimethyl sulphate and employing an atmosphere of hydrogen. After the methylation, the reaction mixture was poured into water, the product (yield 80%) collected, and recrystallized from acetic acid, from which it was obtained in white needles, m.p. 119–120° (found: MeO, 55·7. $C_{12}H_4(MeO)_6$ requires MeO, 55·7%).

6 : 6′-*Dibromo*-2 : 3 : 5 : 2′ : 3′ : 5′-*Hexamethoxydiphenyl*.—A dilute solution of the hexamethoxydiphenyl in chloroform was titrated with a dilute solution of bromine in the same solvent. Decolorization took place instantly, and after evaporation of the solvent, and crystallization of the residue from acetic anhydride, small prismatic crystals were obtained which were very sparingly soluble in ordinary solvents, and had m.p. 271–272° (found: Br, 32·7. $C_{18}H_{20}O_6Br_2$ requires Br, 32·5%).

6 : 6′-*Dinitro*-2 : 3 : 5 : 2′ : 3′ : 5′-*Hexamethoxydiphenyl*.—The finely powdered hexamethyl ether was suspended in a large quantity of acetic acid, and rather more than the theoretical amount of nitric acid diluted with the same solvent added. The solution acquired a brown colour and the methyl ether passed into solution, and was replaced by a precipitate of the nitro-compound. This was collected and purified by crystallization from acetic acid, in which it was very sparingly soluble even when hot. It formed sulphur yellow prisms, m.p. 300–301° (found: N, 6·7. $C_{18}H_{20}O_{10}N_2$ requires N, 6·6%) which gave a dark red colour with concentrated sulphuric acid.

6 : 6′-*Dibromo*-3 : 3′-*dimethoxydiquinone*.—6 : 6′-Dibromo-2 : 3 : 5 : 2′ : 3 : 5′-hexamethoxydiphenyl was introduced in small quantities into cold concentrated nitric acid, any rise in temperature being avoided. The ether dissolved and nitrous fumes were evolved. The reaction mixture was poured into water, and the precipitated quinone crystallized from acetic acid. It formed yellow needles, m.p. 240–242° (decomp.), but began to sinter at 236° (found: Br, 36·4. $C_{14}H_8O_6Br_2$ requires, Br, 37·0%). Dehydrodivanillin is soluble in alkalis to brownish-red solutions and on acidification a brown amorphous substance is precipitated.

Toluquinol.—Toluquinol is easily obtained by reducing toluquinone with sulphur dioxide, but the yield is decreased by the simultaneous formation of sulphonic acid.† A better yield is obtained as follows:—

A solution of stannous chloride (60 gm.) in boiling water was added to an efficiently stirred suspension of toluquinone (30 gm.) in hot water (300 c.c.). The reduction took place instantly and the crude toluquinol (26 gm., 22 gm. after crystallization from toluene) was isolated by means of ether.

Toluquinol Dimethyl Ether.—The methylation was carried out as described by Chapman, Perkin and Robinson‡ for the methylation of pyrogallol. Two molecules of dimethyl sulphate and sodium hydroxide were employed for each hydroxyl group, and the yield under these conditions was almost quantitative.

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† *Cf.* Dodgson, 'J. Chem. Soc.,' p. 2498 (1930).

‡ 'J. Chem. Soc.,' p. 3028 (1927).

5-Nitrotoluquinol Dimethyl Ether.—Nitric acid (d, 1·42; 0·12 gm. mol.) in acetic acid (5-10 vol.) was added to a cooled solution of toluquinol dimethyl ether 0·1 gm. mol.) in acetic acid (5–10 vol.); the solution acquired a brown colour, and the nitro-derivative soon separated. After 15 minutes, water was added and the nitro-derivative collected; the yield was quantitative and the substance was at once obtained in a pure state as sulphur yellow prisms, m.p. 117–118° (found: N, 7·0. $C_9H_{11}O_4N$ requires N, 7·1 %).

5-Iodotoluquinol Dimethyl Ether.—Iodine (15 gm.) and mercuric oxide (13 gm.) were added to toluquinol dimethyl ether (9 gm.), which was stirred during the whole experiment and heated on the steam-bath to 85–95°. When all the iodine had been consumed, the iodo-derivative was extracted with hot benzene, and this solution was shaken with aqueous sodium iodide. The red product, obtained on evaporation of the benzene, was repeatedly crystallized from methyl alcohol in colourless crystals, m.p. 85° (found: I, 45·4. $C_9H_{11}O_2I$ requires I, 45·7%). When dissolved in concentrated nitric acid, iodine was liberated.

2 : 5 : 2′ : 5′-*Tetramethoxy*-4 : 4′-*dimethyldiphenyl.* — (I) 4 : 4′-Ditoluquinone (Nietzki and Bernard, *loc. cit.*) was dissolved in hot acetic anhydride containing a few drops of pyridine and zinc dust added until the yellow colour was discharged. The tetra-acetoxyditolyl was precipitated with water, collected and crystallized from acetic acid, m.p. 137°; Brunner obtained the substance in a similar way and records the m.p. 135°. The tetra-acetate was hydrolysed with dilute methyl alcoholic sulphuric acid and the resulting ditoluquinol was methylated as described above. The tetramethyl derivative was crystallized from methyl alcohol and then distilled in a high vacuum. It melted at 135–136°; Brunner (*loc. cit.*) gives 129°; Fichter and Ris[†] 135–136°.

(II) 4-Iodotoluquinol dimethyl ether (3 gm.) was mixed with copper powder (3 gm.) and heated slowly to 210° while being continuously stirred. The temperature then rose, and rapidly reached 240–245°; the mixture was kept at 230° for 10 minutes and was then extracted with boiling alcohol. On cooling, the tetramethoxyditolyl (yield 80%) separated, and was crystallized from methyl alcohol and distilled in a high vacuum. It had m.p. 135–136°, and a mixed melting point with the previous preparation showed no depression (found: MeO, 40·8. $C_{14}H_{10}(MeO)_4$ requires MeO, 41·0%). Exposure to bromine vapour produced a greenish-brown coloration.

Spica's "Toluquinone Polymeride."—A mixture of toluquinone (20 gm.) sulphuric acid (50 gm.), and water (5 gm.), was kept at the room temperature for 24 hours. The brownish-black deposit was washed with water until free from sulphuric acid, then dried, dissolved in acetic acid, and reprecipitated with water. The substance thus obtained was dried and extracted with chloroform; a small amount (0·2–0·4 gm. in different experiments) of the violet substance described by Spica (*loc. cit.*) was thus isolated.

[†] 'Helv. Chim. Acta,' p. 812 (1924).

It was easily converted into 4 : 4'-dimethyldiquinone on oxidation with nitric or chromic acids. Reductive acetylation yielded an acetate, m.p. 137°, which showed no depression when mixed with the acetate obtained on reductive acetylation of ditoluquinone.

The product obtained by treatment of toluquinone with sulphuric acid for 10 hours was a mixture of unchanged toluquinone, toluquinhydrone, Spica's polymerids and a small amount of the termolecular product which is described on p. 237. After treatment for 24 hours, the toluquinone and the toluquinhydrone had disappeared almost completely, and after 48 hours only traces of Spica's polymeride could be detected, the products of reaction being amorphous substances and the termolecular polymeride. After 3 days, Spica's polymeride had disappeared completely.

2 : 2'-Diethoxy-5 : 5'-dimethoxy-4 : 4'-dimethyldiphenyl. — The reduction of Nietzki's quinone with sulphur dioxide proceeds slowly but is very much facilitated by the addition of pyridine. This phenomenon is not peculiar to this compound; it is very general and has also been observed in reductive acetylations.

Sulphur dioxide was passed rapidly through a solution of Nietzki's quinone (10 gm.) in boiling alcohol and after decolorization, water was added to turbidity, and the mixture kept overnight in an atmosphere of sulphur dioxide. The precipitated phenol was collected and dried over sulphuric acid.

A mixture of the phenol (5·5 gm.), ethyl iodide (13 gm.) and a solution of sodium (1·9 gm.) in alcohol (40 c.c.) was refluxed for 2 hours in an atmosphere of nitrogen. The mixture was then poured into water, the oily ethyl derivative was taken up in ether, and the extract shaken with alkali and dried over magnesium sulphate. The oil remaining on evaporation rapidly crystallized in colourless prisms when stirred with light petroleum. The substance was purified by recrystallization from methyl alcohol and distillation in a high vacuum, m.p. 116–118° (found: C, 72·6; H, 7·9. $C_{20}H_{26}O_4$ requires C, 72·7; H, 7·9%) unchanged by recrystallization from acetic acid. A brownish-green coloration was produced on exposure to bromine vapour.

Toluquinol Diethyl Ether.—A mixture of toluquinol (12·4 gm.), ethyl iodide (46·8 gm.) and a solution of sodium (6·9 gm.) in alcohol (60 c.c.) was refluxed for 2 hours under nitrogen. After isolation the ethyl ether thus obtained (12 gm.) was oxidized with chromic acid to the coupled quinone described by Noelting and Werner (*loc. cit.*).

2 : 2′-*Dimethoxy*-5 : 5′-*diethoxy*-4 : 4′-*dimethyldipehnyl*. — A solution of Noelting's quinone (10 gm.) in alcohol (20–30 c.c.) containing a few drops of pyridine was refluxed in a stream of sulphur dioxide until colourless. Carbon dioxide was passed in order to remove the sulphur dioxide, and the phenol was methylated in an atmosphere of hydrogen with dimethyl sulphate and caustic soda, using three times the theoretical quantities of the reagents. The methyl derivative formed colourless prisms, m.p. 94–96° (found: C, 73·0; H, 8·0. $C_{20}H_{26}O_4$ requires C, 72·7; H, 7·9%). This methyl ethyl ether crystallizes much more readily than the higher melting isomeride, and like the latter compound it is oxidized by nitric acid to ditoluquinone and exhibits the bromine reaction.

2(?) : 3 : 6 : 2′(?) : 3′ : 6′-*Hexa-acetoxy*-4 : 4′-*dimethyldiphenyl*.—A mixture of ditoluquinone (5 gm.), acetic anhydride (30 c.c.) and sulphuric acid (1·5 c.c.) was kept for 24 hours at 20–30°. After this time the diquinone was completely converted into hexa-acetate. The mixture was poured into water and the almost pure product (yield, 96%) collected and crystallized from acetic acid in colourless needles, m.p. 202–203° (found: C, 58·5; H, 5·0. $C_{26}H_{26}O_{12}$ requires C, 58·9; H, 4·9%). It was sparingly soluble in the usual solvents except acetone. The phenol obtained by hydrolysis with alcoholic sodium hydroxide absorbed oxygen yielding a permanganate-coloured solution.

Addition of Hydrogen Chloride to Ditoluquinone.—Hydrogen chloride was passed through a suspension of ditoluquinone in chloroform when the initial brown coloration gradually disappeared. The nearly colourless solution was concentrated in a vacuum over paraffin wax and sodium hydroxide, the red-brown crystals were collected and washed with methyl alcohol, yielding a colourless product. This chlorophenol was instantly decomposed by alkali, the green solution rapidly turning brown. On attempting to crystallize the chlorophenol from dilute alcohol, hydrogen chloride was liberated and a violet quinonoid substance formed. The properties of this chlorophenol thus correspond to those of the analogue derived from 4 : 4′-dimethoxydiquinone.

Aminoquinol Dibenzyl Ether.—Iron powder was added to nitroquinol dibenzyl ether (10 gm.)† dissolved in boiling acetic acid (30 c.c.) until the yellow colour had disappeared. The reaction mixture was poured into water, the solid dissolved in chloroform and the solution shaken with alkali, dried and evaporated. The amine was recrystallized from methyl alcohol, and obtained as colourless rhombic plates, m.p. 100–102° (found: N, 4·9. $C_{20}H_{19}O_2N$ requires N, 4·6%). On attempted diazotization, brown or blue-black products were obtained.

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† Schiff and Pellizzani, 'Liebig's Ann.,' vol. 221, p. 364 (1883); Colson, 'Bull. Soc. Chim.,' (3), I., p. 348 (1889).

Acetyl Derivative.—The acetyl derivative was obtained by short treatment with boiling acetic anhydride; it formed colourless needles, m.p. 86–87° when recrystallized from methyl alcohol (found: N, 4·0. $C_{22}H_{21}O_3N$ requires N 4·2%).

p-*Nitrobenzylidene Derivative.*—The amine and *p*-nitrobenzaldehyde were fused together until no more water was evolved. After recrystallization from methyl alcohol the Schiff's base formed yellow needles, m.p. 105° (found: N, 6·7. $C_{27}H_{22}O_4N_2$ requires N, 6·4%).

p-*Nitrobenzylidene Derivative of 2-Iodo-4-nitroaniline.*—Iodonitraniline (8 gm.) was heated at 130–150° with *p*-nitrobenzaldehyde (5 gm.) during 15 minutes. After cooling, the solid was extracted with boiling alcohol, and the residual yellow substance was recrystallized from nitrobenzene or pyridine in yellow needles, m.p. 194–196° (found: I, 31·6. $C_{13}H_8O_4N_3I$ requires I, 32·0%).

m-*Nitrobenzylidene Derivative of 2-Iodo-4-nitroaniline.*—The *m*-nitrobenzylidene derivative was prepared in the same way as the *p*-isomeride, and formed yellow needles, m.p. 177–178° (found: I, 31·3; N, 10·8. $C_{13}H_8O_4N_3I$ requires I, 32·0; N, 10·6%).

It was not possible to couple these iodo-derivatives by means of copper powder to the corresponding diphenyl derivatives.

Studies on the Formation of Complex Oxidation and Condensation Products of Phenols. Part III.—*Rearrangements of Oxidation-Reduction Type in the Diquinone Group.*

By H. G. H. Erdtman.

(Communicated by R. Robinson, F.R.S.—Received 27 January, 1933. Revised 31 July, 1933.)

The diquinones have been but little investigated, and as they contain two condensed highly active quinonoid systems it is to be anticipated that they should be capable of interesting intramolecular reactions.

When heated to 210–215°, 4 : 4′-dimethoxydiquinone is rapidly converted into a red crystalline isomeride (yield, 90%), soluble in alkali with an intense blue colour, and yielding a mono-acetate indicating the occurrence of a free hydroxyl group. Two hydrogen atoms are taken up on reduction, and the phenolic product yields a triacetate and a trimethyl ether. It follows that of the four carbonyl oxygens of 4 : 4′-dimethoxydiquinone, one has been converted into a hydroxyl group, and another which does not exhibit any functional activity, is probably present as ethereal oxygen. These results led to formula (III) as representing the product of rearrangement.

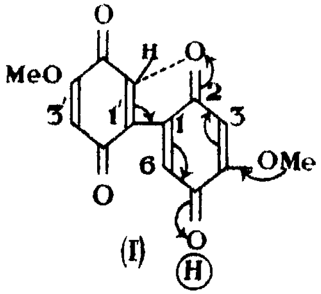
The same substance is obtained at a lower temperature in the presence of acids. Thus, it is formed during the recrystallization of 4 : 4′-dimethoxydiquinone from acetic acid, and it has been observed as a by-product of the thermal decomposition of the addition product of hydrogen chloride and dimethoxydiquinone by hot acetic anhydride. It is slowly formed as a by-product of the Thiele acetylation of 4 : 4′-dimethoxydiquinone at ordinary temperature. (*Cf.* p. 212.)

The fact that acids facilitate the reaction suggests that it is initiated by the attraction of a proton to the carbonyl oxygen at 5 (I), which causes an electron deficiency at 6′. The hydrogen atom in the latter position is liberated as a proton by contributing one of its electrons to the oxide link under formation (II).

An alternative to this mechanism, which may occur when pure, dry 4 : 4′-dimethoxydiquinone undergoes rearrangement when heated, is a chain reaction, in which the carbonyl oxygen at C 5 in one molecule acts as acceptor, and the carbon atom 6′ in another as donor, of protons.

4 : 4′-Dimethyldiquinone undergoes the same rearrangement, but the yield is extremely low, since most of the ditoluquinone is converted into a brown amorphous substance. This is undoubtedly due to the much weaker polarization of the carbonyl double bond at C 2, as compared, for example, with that which occurs in 4 : 4′-dimethoxydiquinone (CH_3- instead of CH_3O- in the 4-positions).

A similar reaction probably occurs in the conversion of diquinizaryl into a furane derivative on heating with nitronaphthalene.*



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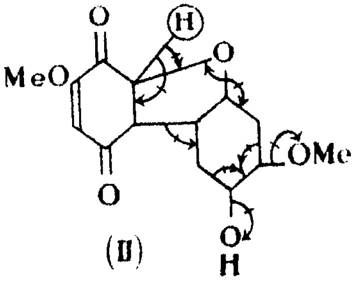

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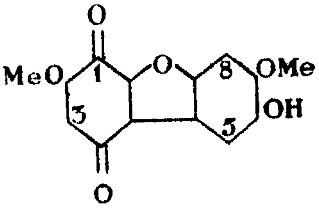

(III)

Experimental.

Rearrangement of 4 : 4′-*Dimethoxydiquinone.*

6-*Hydroxy*-2 : 7-*dimethoxydiphenyleneoxidequinone* (1 : 4). — α-Bromonaphthalene was saturated at 200° with pure dimethoxydiquinone and the temperature was then maintained at 250–280° for a few minutes. On cooling, the new substance crystallized, and the bromonaphthalene was removed by light petroleum. The product (yield, 90%) was then washed with methyl alcohol, and crystallized from nitrobenzene in red needles having a strong surface lustre and sintering at 242°, m.p. 250° (found: C, 61·3; H, 3·6; MeO, 22·6.

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* Schmidt, Stein and Bamberger, 'Ber. deuts. chem. Ges.,' vol. 63, p. 300 (1930).

$C_{12}H_4O_4(MeO)_2$ requires C, 61·3; H, 3·7; MeO, 22·6%). (The melting point is difficult to observe owing to the intense colour.) The substance was sparingly soluble in most low-boiling solvents, although acetone and pyridine dissolve it to red solutions. It was slowly reduced by phenylhydrazine with evolution of nitrogen.

Monoacetate.—Short boiling with acetic anhydride yields the monoacetate which crystallized from acetic acid in scarlet prisms, m.p. 252–254° (found: MeO, 19·1. $C_{12}H_3O_3(MeO)_2OAc$ requires MeO, 19·6%).

1 : 4 : 6-*Trihydroxy*-2 : 7-*dimethoxydiphenylene Oxide.*—The product of rearrangement of 4 : 4′-dimethoxydiquinone was easily reduced by means of zinc dust in a hot acetic acid solution, which was filtered and poured into water containing sulphurous acid. After 12 hours a very voluminous jelly had separated, but this, when heated with acetic acid, was dehydrated and transformed into small white, very sparingly soluble needles. After crystallization from a large volume of acetic acid, the product was obtained as long thread-like needles which decomposed at about 210° (found: C, 57·9; H, 4·8; MeO, 20·6. $C_{12}H_3O(MeO)_2(OH)_3$ requires C, 60·9; H, 4·4; MeO, 22·5%). It was difficult to free the substance from ash, and this may account for the unsatisfactory analytical figures.

Triacetate.—The triacetate of the reduction product is easily obtained by short heating with acetic anhydride and pyridine, or better by reductive acetylation of the product of rearrangement. After recrystallization from acetic anhydride or *n*-butyl alcohol, the acetate formed long, thin, white needles, m.p. 232–233° (found: C, 59·7; H, 4·7; MeO, 15·6. $C_{12}H_3O(MeO)_2(OAc)_3$ requires C, 59·7; H, 4·5; MeO, 15·4%). It dissolves in sulphuric acid to a deep permanganate-coloured solution and it is readily hydrolysed by alcoholic alkali yielding a blue solution as the result of oxidation.

Tri-p-*nitrobenzoyl Derivative.*—A mixture of *p*-nitrobenzoyl chloride (4·5 mol.) and 1 : 4 : 6-trihydroxy-2 : 7-dimethoxydiphenylene oxide (1 mol.) in 10 times their combined weight of pyridine was refluxed for 1 hour. The ester separated as a fine yellow powder. The reaction mixture was poured into water and the crude substance (almost quantitative yield) washed with alcohol and ether and crystallized from α-bromonaphthalene in small yellow needles, m.p. above 300° (found: MeO, 8·5; N, 5·6. $C_{12}H_3O(C_6H_4NO_2CO_2)_3(OMe)_2$ requires MeO, 8·6; N, 5·8%).

1 : 2 : 4 : 6 : 7-*Pentamethoxydiphenylene Oxide.*—A mixture of 1 : 4 : 6-triacetoxy-2 : 7-dimethoxydiphenylene oxide (3·5 gm.), 2% methyl alcoholic sulphuric acid (50 c.c.) and a little zinc dust was refluxed for a short time in an atmosphere of hydrogen. The free acid was then neutralized with sodium

hydroxide solution and the phenol methylated following the method of Chapman, Perkin, and Robinson (*loc. cit.*). The reaction mixture was poured into water, and the grey precipitate (2·3–2·5 gm.) dried and recrystallized from acetic acid or methyl alcohol. From acetic acid a poor yield of the pure pentamethyl ether (m.p. 109–110°) is obtained, whereas from methyl alcohol, a greater yield is obtained, but the product (m.p. 103–106°) is not quite pure (found: C, 63·9; H, 5·8; MeO, 48·6. $C_{12}H_3O(MeO)_5$ requires C, 64·2; H, 5·7; MeO, 48·7%).

The pentamethyl ether is slightly soluble in ether, moderately soluble in acetic acid and acetic anhydride, and easily soluble in acetone, chloroform, pentachloroethane, and pyridine. Concentrated sulphuric acid dissolves it with a brown coloration which rapidly changes to red-violet. With nitrous fumes it gives a violet coloration, and concentrated nitric acid attacks it vigorously.

Rearrangement of the Coupled Product from Methoxyquinone.—This experiment was carried out in order to determine whether any appreciable amount of 4 : 4′-dimethoxydiquinol is formed during the reaction. When the product obtained on heating the coupled product of methoxyquinone with α-bromonaphthalene was subjected to reductive acetylation, large amounts of the furane derivative could be isolated, together with a considerable quantity of amorphous matter. Only a minute amount of 4 : 4′-dimethoxydiquinol tetra-acetate could be isolated.

6-*Hydroxy*-2 : 7-*dimethyldiphenyleneoxidequinone* (1 : 4).—4 : 4′-Dimethyldiquinone was heated for 10 minutes in α-bromonaphthalene at 220° (not higher). On cooling an amorphous red powder was precipitated and this was collected, washed with ligroin, and extracted with a large volume of hot light petroleum (b.p. 100–120°). A bright brick-red powder separated on cooling and was recrystallized from toluene, forming beautiful red needles, m.p. 218–220° (found: C, 68·4; H, 4·7. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·1%). The yield was very poor (4–6%), and owing to lack of material complete purification was impossible. This substance exhibits properties closely analogous to those of the corresponding product of rearrangement of 4 : 4′-dimethoxydiquinone. It gives a blue solution in alkali, which becomes violet and then brown when shaken with air. By contrast, the product of the rearrangement of dimethoxydiquinone is very stable towards oxygen. This diphenylene oxide derivative is not an intermediate between ditoluquinone and the amorphous products of its thermal polymerization, since it may be boiled with α-bromonaphthalene for a long time without suffering any change.

Reductive Acetylation of the crude product of the thermal polymerization and rearrangement of ditoluquinone gave a grey product, which was purified by extraction with light petroleum and subsequent recrystallization from acetic acid. This substance, needles, m.p. 168–171°, was easily hydrolysed to a blue solution by alcoholic sodium hydroxide, and was, therefore, 1 : 4 : 6-triacetoxy-2 : 7-dimethyldiphenylene oxide (found : C, 64·6 ; H, 4·9. $C_{20}H_{18}O_6$ requires C, 67·8 ; H, 5·1%). The amount available was not sufficient to permit a rigorous purification. From the mother liquor a minute amount of 4 : 4′-dimethoxydiquinoltetra-acetate was isolated and identified by mixed melting point (137°) with an authentic sample.

When heated with α-bromonaphthalene dibenzoquinone yielded an amorphous red substance, but no product of rearrangement could be isolated.

Summary of Parts II and III.

The mechanisms of the oxidative coupling of phenols and the coupling of quinones are discussed.

The oxidation of pyrogallol in alkaline solution (baryta) yields 2 : 3 : 4 : 2′ : 3′ : 4′-hexahydroxydiphenyl. The validity of the constitution assumed was proved by direct synthesis.

All bis-hydroxyquinols obtained by oxidative coupling of hydroxyquinols and their derivatives, hitherto described in the literature belong to the 2 : 4 : 5 : 2′ : 4′ : 5′-hexahydroxydiphenyl series.

Methoxyquinone couples quantitatively in the presence of mineral acids to form a partially oxidized 2 : 4 : 5 : 2′ : 4′ : 5′-hexahydroxydiphenyl.

Oxidation of this compound gives 4 : 4′-dimethoxydiquinone, which has been studied in regard to its addition reactions.

The addition of hydrogen chloride to 4 : 4′-dimethoxydiquinone is reversible.

In acid solutions hydroxyquinol trimethyl ether is easily dehydrogenated to 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethoxydiphenyl, but under certain conditions can yield an " indigoid " quinone.

Bis-hydroxyquinol derivatives of the 2 : 3 : 5 : 2′ : 3′ : 5′-hexahydroxdiphenyl series have been prepared synthetically, and their reactivity has been studied.

The chemical properties of toluquinone are closely analogous to those of methoxyquinone, which is, however, more reactive.

Toluquinone couples in acid solution to form a partially oxidized 4 : 4′-dimethyldiquinol which can undergo further condensations.

The quinonoid coupled product obtained by oxidizing toluquinol dimethyl ether with chromic acid has definitely been proved to be of the indigoid type.

When heated, 4 : 4′-dimethoxy and 4 : 4′-dimethyldiquinone yield products of rearrangement which are quinonoid diphenylene oxide derivatives.

Studies on the Formation of Complex Oxidation and Condensation Products of Phenols. Part IV.—Termolecular Polymerization Products of p-*Benzoquinone, Toluquinone, and α-Naphthoquinone.*

By H. G. H. Erdtman.

(Communicated by R. Robinson, F.R.S.—Received 27 January, 1933. Revised 31 July, 1933.)

During the investigation of the "toluquinone polymeride" of Spica (p. 219) it was observed that the fraction which is insoluble in chloroform contains a large quantity of a crystalline phenolic substance.

The substance has the empirical formula $C_{21}H_{16}O_4$, and the determination of the molecular weight of its dimethyl ether showed that the compound was monomolecular. Of the two oxygen atoms only two exhibit phenolic functions; the others do not react with carbonyl reagents, and must consequently be present as ethereal oxygen.

Before we proceed to consider the constitution of this peculiar product of polymerization, a few matters arising from related studies must be discussed briefly. Recently Oesterlin,[*] and Goldschmidt, Schültz and Bernard,[†] have synthesized phenolic substances containing several benzene rings linked up in a chain by means of oxygen atoms; these substances exhibit properties which are different from those of the product under discussion. For example, the melting points of derivative in the group of polyphenyl ether of approximately the same molecular magnitude are much lower. Further, the stability of such systems seems to be inferior to that of the polymerization product of toluquinone.

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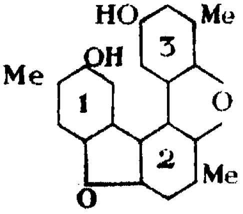
[*] 'Mhft. Chem.,' vol. 57, p. 31 (1931).

[†] 'Liebig's Ann.,' vol. 478, p. 1 (1930).

As has been noted above, methoxyquinone and toluquinone undergo coupling to diphenyl derivatives in acid solution. Methoxyquinone couples almost instantly and quantitatively to the partially oxidized dimethoxydiquinol, and no termolecular products have been obtained. Toluquinone, on the other hand, couples very slowly, and at the beginning of the reaction there exist simultaneously in the reaction mixture toluquinone, toluquinhydrone, Spica's dimolecular coupled product, and a small amount of the termolecular substance. After some time, however, the mono- and dimolecular substances disappear, and only termolecular and amorphous products are present. It would thus seem that the diphenyl derivative may be an intermediate product in the formation of the termolecular compound. If this is correct, it is obvious that the ethereal oxygen atoms must be of the diphenylene oxide type. It is known that diquinols easily undergo dehydration to diphenylene oxides, examples being the dehydration of bis-hydroxyquinol (p. 198) and of ditoluquinol.* These substances are characterized by great stability, high melting points, and low solubility, and they usually become strongly electrified when rubbed. These properties are all exhibited very markedly by the product of polymerization of toluquinone, and accepting the view that the ether oxygens occur in furane nuclei, the following formulæ alone account for the composition and the properties of the compound :



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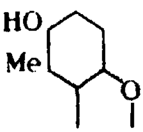

(II)

It is noteworthy that the anhydroditoluquinol of Nietzki crystallizes with $1H_2O$. The present bisanhydrotritoluquinol possessing two furane nuclei crystallizes with $2H_2O$. The rings 1 and 2 represent the initial coupled product of toluquinone (" Spica's polymeride "). It is improbable that ring 3 is attached to the ditolyl system through the carbon atom in the *p*-position to the methyl group, because the methyl ether of bisanhydrotritoluquinol easily undergoes bromination and nitration yielding monosubstituted products. This position is known to be highly anionoid (*cf.* p. 204). An alternative arrangement of ring 3 is shown in II, but this corresponds less closely with the known facts regarding the reactivity of toluquinone towards ketones, Grignard reagents, etc.

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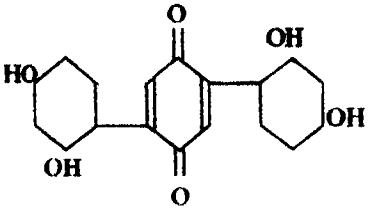
* Nietzki, 'Liebig's Ann.,' vol. 215, p. 166 (1882).

Several other quinones besides toluquinone yield crystalline products of polymerization when treated with acids or when heated alone. Liebermann* investigated the polymerization of benzoquinone with sulphuric acid and tried unsuccessfully to characterize the product obtained by distillation over zinc dust. Applying the technique developed for the preparation of the toluquinone polymeride, the present author succeeded in converting *p*-benzoquinone into a crystalline termolecular substance in about 4% yield. The acetate had the composition $C_{22}H_{14}O_6$ corresponding to a diacetate of bis-anhydrotriquinol: $C_{18}H_8O_2(OCOCH_3)_2$. On hydrolysis with sulphuric acid in acetic acid, the phenol $C_{18}H_{10}O_4$ was obtained, and on methylation yielded the dimethyl ether $C_{18}H_8O_2(OCH_3)_2$.

Pummerer and co-workers† have shown that in presence of aluminium chloride or, occasionally, dilute sulphuric acid, *p*-benzoquinone easily reacts with aromatic hydrocarbons and phenols yielding terphenyl derivatives. Thus, benzoquinone and resorcinol yielded the quinhydrone corresponding to (III):



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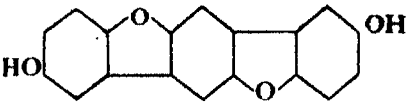

(IV)

Kögl‡ proved that the products obtained in these condensations are 2 : 5-disubstituted *p*-benzoquinones, and since the polymerization of *p*-benzoquinone is accompanied by the formation of a large amount of quinol (about 50%), it is evident that the bis-anhydrotriquinol is closely related to the condensation products described by Pummerer. The following structure is therefore assigned to the termolecular substance obtained from *p*-benzoquinone:

As has been already mentioned, this product is obtained in poor yield, but toluquinone affords about 30% of the corresponding termolecular compound.

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* 'Ber. deuts. chem. Ges.,' vol. 18, p. 966 (1885).

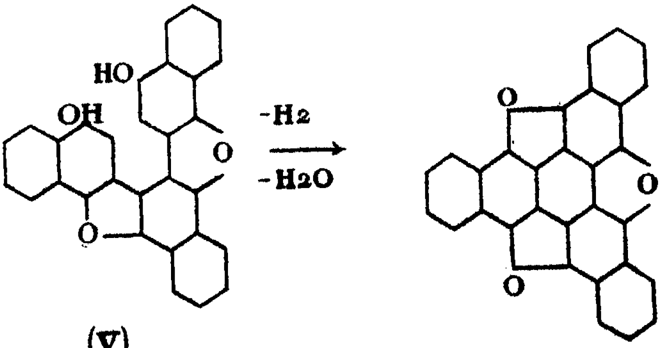
† 'Ber. deuts. chem. Ges.,' vol. 55, p. 3105 (1922); vol. 60, p. 1441 (1927); *cf.* also Adams, 'J. Amer. Chem. Soc.,' vol. 53, p. 343 (1931).

‡ 'Liebig's Ann.,' vol. 447, p. 448 (1926).

The great difference between the two processes is certainly due to the hindering of further polymerization by the methyl group. It was therefore of interest to study the polymerization of xyloquinones, and especially of *o*-xyloquinone.

o-Xyloquinone is not readily accessible, and therefore α-naphthoquinone was chosen as a substitute (*cf.* Liebermann, *loc. cit.*). On polymerization with sulphuric acid crystalline substances were obtained in about 70% yield. It may be mentioned here that the polymerization products of benzoquinone and toluquinone offer very great difficulties as regards isolation and purification because of their insolubility. These difficulties are greatly increased with α-naphthoquinone and the problem is still further complicated by the fact that the crystalline product is not homogeneous, but consists of a mixture of at least two substances. The author, therefore, has confined himself to an attempt to isolate and characterize these compounds, but has not dealt with the relative amounts of the different products, the preparation of derivatives and related problems. It is interesting that α-naphthoquinone yields the same products when mixed with α-naphthoquinol and treated with sulphuric acid; dinaphthoquinol derivatives could not be obtained in this way.

On acetylation the crude polymerization product of α-naphthoquinone yields a crystalline mixture of substances, one of which is sparingly soluble in boiling quinoline, and the other insoluble. The soluble component was purified by recrystallization from the same solvent and sublimation in a high vacuum.



(V) (VI)

It had the composition $C_{34}H_{20}O_6$, which corresponds to a diacetate of a bisanhydrotrinaphthoquinol, and the substance is so similar to the acetate of the toluquinone and benzoquinone polymerization products, that an analogous structure for the phenol (V) must be assumed, although its dihydric nature has not yet been directly proved.

The insoluble product is crystalline, neutral, and does not give any colour reaction with sulphuric acid. It is very sparingly soluble in boiling β-naphthylamine (b.p. 306°), and the only method of purification which was found practicable was sublimation in a very high vacuum. It was very difficult to free it completely from the quinoline-soluble product by extractions with that solvent, or even with naphthylamine, but at a temperature of about 300° the more soluble substance sublimed alone. The residue sublimed at a much higher temperature (400–500°). The composition of the latter compound is $C_{30}H_{12}O_3$, and it is almost certainly trinaphthobenzenetrioxide (VI), derived from the parent phenol of the quinoline-soluble acetate by dehydrogenation and loss of water.

It is very difficult to form any detailed opinion on the mechanism leading to these termolecular furanoid compounds. It is probable, however, that triquinols are first formed, and then undergo further coupling with unchanged quinone or with quinonoid coupled products yielding high-molecular amorphous substances (" humic acids ") or alternatively stabilize themselves by dehydration and yield the furanoid structures, which are no longer capable of quinone formation. The problem is very complex and much more experimental work is needed ; the investigation in this field is being continued.

EXPERIMENTAL.

Polymerization of p-*Benzoquinone with Sulphuric Acid.*

Diacetoxytriphenylene Dioxide.—A solution of benzoquinone (100 gm.) in warm acetic acid (500 c.c.) was cooled until the quinone began to crystallize ; a cold mixture of concentrated sulphuric acid (250 c.c.) and water (750 c.c.) was then added, and the mixture vigorously shaken mechanically for 2·5 days when scarcely any unchanged quinone could be detected. The thick, blue-black precipitate was collected, washed thoroughly with water, and dried in the air and over sulphuric acid in a vacuum. It consisted of a brownish-black powder (B, see p. 235) (50 gm.) with a violet reflex. The filtrate contained quinol (about 50 gm.) which was isolated by extraction with ether, and identified by melting point and by conversion into benzoquinone.

The polymerization product and an excess of zinc dust were gradually introduced into a stirred mixture of acetic anhydride (150 c.c.) and pyridine (10–15 c.c.). The faintly brown solution, which had become very hot during the reduction, was filtered and very soon the impure acetate of the termolecular condensation product began to separate from the filtrate. After 2 days this substance (A) (5–6 gm.) was collected and washed with acetic acid, water, alcohol, and ether. The filtrate from (A) was poured into water, and yielded a large quantity of a faintly yellow, amorphous powder (C, see p. 235).

The crude polymerization product (A) which had a faint greenish colour was distinctly crystalline under the microscope, but was very difficult to purify by recrystallizations from ordinary organic solvents. Ultimately the following procedure proved suitable. The crude substance was slowly stirred into molten paraffin wax (100 c.c.) heated to 210–220°. The acetate passed into solution, and a layer of a black gum was deposited on the bottom of the vessel. When a clear solution was obtained, the paraffin solution was allowed to solidify, the layer of impurities excised, and the wax dissolved in ligroin. The purified dihydroxytriphenylene dioxide diacetate remained undissolved in the form of snow-white, thread-like crystals, m.p. 225–230° very similar to cotton wool (found: C, 71·2; H, 3·8. $C_{22}H_{14}O_6$ requires C, 70·6; H, 3·7%). Recrystallization from paraffin or pyridine did not raise the m.p.; the melt was not quite colourless, but slightly yellow. For complete purification, the substance was sublimed in a high vacuum (0·0003 mm. of mercury) at a temperature of 240°. It sublimed rapidly in a snow-white crystalline state and the purified material was crystallized once from acetic anhydride, and had m.p. 236–237° (found: C, 70·3; H, 3·8. $C_{22}H_{14}O_6$ requires C, 70·6; H, 3·7%). It was sublimed and recrystallized twice from acetic anhydride, but neither melting point nor composition was altered. This substance is insoluble in cold organic solvents, sparingly soluble in boiling acetic anhydride—and pyridine, and rather easily soluble in boiling quinoline and paraffin. When ground in a mortar it becomes highly electrified. It dissolves in concentrated sulphuric acid without developing any characteristic colour.

Dihydroxytriphenylene Dioxide (IV).—A suspension of the pure acetate (2–3 gm.) in acetic acid (50 c.c.) containing sulphurous acid (1 c.c.) was refluxed in an atmosphere of hydrogen* until a solution was obtained which yielded no precipitate with dilute sodium hydroxide (about 0·5 hour). Hot water was gradually added to precipitate the phenol, which was collected, washed with water and dried.

Dihydroxytriphenylene dioxide consisted of long threads having a pale blue colour as the result of superficial oxidation. After recrystallization from a mixture of 2 parts of alcohol and 1 part of water (charcoal) it melted at 336–340° (found in material dried at 130° over phosphoric anhydride in a vacuum:

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* When the hydrolysis was carried out in the presence of air a deep blue amorphous substance was obtained.

C, 74·2; H, 3·5. $C_{18}H_{10}O_4$ requires C, 74·5; H, 3·5%). This substance is insoluble in chloroform and benzene, very soluble in acetone, pyridine, hot alcohol and acetic acid. It sublimes in a high vacuum with partial decomposition. Its alcoholic solution yields a red azo-dye with diazotized sulphanilic acid. The original di-acetate is obtained by treatment with acetic anhydride and pyridine.

Dimethoxytriphenylene Dioxide.—Dimethyl sulphate (10 c.c.) followed by 40% sodium hydroxide solution (10 c.c. in drops) were added to a filtered (charcoal) alcoholic solution of the crude phenol (IV) (2–3 gm.), which was stirred mechanically in an atmosphere of hydrogen. After the addition of part of the alkali, the crystalline methyl ether suddenly began to separate, and at the conclusion of the methylation the reaction mixture was poured into water, the solid (long needles) m.p. 195–200°, collected and washed successively with water, alcohol, and ether. Recrystallization from pyridine did not raise the m.p., but one sublimation in a high vacuum yielded material, m.p. 207–208° after sintering at 200° (found: C, 75·0; H, 5·3. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%). Recrystallization of this material from a large quantity of equal volumes of pyridine, acetic acid, and water (charcoal) followed by two sublimations yielded pure dimethoxytriphenylene dioxide, m.p. 210–211° (found: C, 75·6; H, 4·4; M (Rast in camphor), 333, 338. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%; M, 318). Further sublimations did not alter the melting point or the composition. In its physical properties the dimethyl ether closely resembles the diacetate. The methoxyl estimation was extremely difficult; both macro- and micro-Zeisel estimations gave negative results. The analysis was ultimately successful in the micro-methylimide apparatus, but even after boiling the hydriodic acid for 1 hour not even traces of silver iodide were obtained. At a temperature of about 300°, however, when the acid had been distilled silver iodide was precipitated. A second distillation was negative (found: MeO, 18·1; 19·0. $C_{18}H_8O_2(OMe)_2$ requires MeO, 19·5%).

? *Dibromodimethoxytriphenylene Dioxide.*—A small amount of the pure methyl ether was dissolved in a large quantity of chloroform, and obtained as a fine suspension by rapid cooling. To this a dilute solution of bromine in the same solvent was added very cautiously, the decolorization of the bromine proceeded slowly, and the methyl ether dissolved and was at once replaced by a precipitate of long silky needles of the bromo-derivative. A slight excess of bromine was added, and after 2 hours the precipitate was collected and recrystallized from pyridine, in which it is very sparingly soluble. This product decomposed at about 300°, and was not affected by one sublimation in a high vacuum at 290° (found: Br, 30·0; $C_{20}H_{12}O_4Br_2$ requires Br, 33·5%). This substance is very probably a slightly impure dibromo-derivative, but the small amount available prevented complete purification.

Diresorcylquinol Hexamethyl Ether.—This compound, which was prepared in order to compare the properties of a polymethoxyterphenyl with those of the preceding oxidic compounds, was obtained by methylation of the quinol* by the method used for the dihydroxytriphenylene dioxide. The hexamethyl ether, m.p. 156°, crystallized from acetic acid or petroleum (b.p. 100–120°) (found: C, 70·7; H, 6·5. $C_{24}H_{26}O_6$ requires C, 70·3; H, 6·3%). It is sparingly soluble in cold ether and alcohol, very soluble in chloroform, acetone, ethyl acetate, and benzene.

The Amorphous Products of the Polymerization of p-*Benzoquinone with Sulphuric Acid.*—The crude polymerization product B (see p. 232) of quinone exhibits quinonoid properties. It decomposes phenylhydrazine, yielding nitrogen and a dirty brownish yellow "leuco-derivative."

The fitrate from the diacetoxytriphenylene dioxide (A, see p. 233) obtained by reductive acetylation of the crude product of polymerization yielded a large quantity of an amorphous yellow powder (C, see p. 233). This is by no means homogeneous, but can be divided into fractions by solution in different solvents. A very similar product is obtained when quinhydrone instead of quinone is polymerized by sulphuric acid, but in this reaction no termolecular compound could be isolated. As it is of some interest to compare these preparations with the dihydroxytriphenylene dioxide and with some products of the polymerization of *p*-benzoquinone by means of alkali, a few results may be recorded here.

The crude amorphous "leuco-acetate" (C, above) of the quinone polymerization product was dissolved in hot butyl alcohol, the solution cooled, and the amorphous precipitate collected and washed with methyl alcohol and ether. This process was repeated twice, and the material thus "purified" formed a pale yellow, amorphous powder which became strongly electrified on being rubbed. It sintered at 175° and melted at 180–185° to a black liquid (found in material dried in a high vacuum at 125° over P_2O_5: C, 66·5; H, 3·9%).

Another sample of the crude acetate was slowly added to hot paraffin (200°). A large amount of black tar remained undissolved, the liquid was decanted, and on cooling deposited a yellowish white powder. This treatment was repeated, and the solid dissolved as far as possible in a small volume of ether, and precipitated from the filtered solution by petroleum ether. It formed a highly electrified, greyish yellow powder melting at 180–200° to a brown liquid (found in material dried at 125° over P_2O_5: C, 67·9; H, 4·0%).

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* Pummerer and Huppmann, 'Ber. deuts. chem. Ges.,' vol. 60, p. 1442 (1927).

The Amorphous Products of the Polymerization of p-*Benzoquinone with Alkali.*

When a solution of sodium hydroxide (1 gm.) in water (60 c.c.) was added to benzoquinone (2·7 gm.) in total absence of air, the quinone instantly decomposed yielding a deep green solution. After some hours the solution was acidified with dilute sulphuric acid, and the red-brown humic acid which separated was collected, and washed with dilute sulphuric acid. It dissolved in alkali with a green colour, but on absorbing oxygen the solution rapidly became deep brown. Concentration of the filtrate and extraction with ether yielded quinol (0·66 gm.). Under these conditions, therefore, about one molecule of quinol is formed from four molecules of quinone.

Reductive Acetylation of "Quinone Humic Acid."—Dilute sodium hydroxide solution (0·05 gm. mol. NaOH in 50 c.c. water) was added to a suspension of benzoquinone (0·1 gm. mol.) in air-free water (200 c.c.) in an atmosphere of hydrogen. After 2 hours the green solution was acidified with hydrochloric acid, and the humic acid collected and washed with water until marked dispersion took place. The substance was then dehydrated to some extent on porous porcelain, and then dissolved in absolute alcohol at 50°. The solution was repeatedly dried with anhydrous sodium sulphate and finally evaporated below 70° in a vacuum. The resulting thick mass was dissolved in absolute alcohol, dried with sodium sulphate, and obtained as a semi-solid product by evaporation as before. This was dissolved in equal volumes of acetic acid and acetic anhydride containing a little pyridine, and the deep brown solution was stirred with zinc dust in small portions below 60°. The colour of the solution became lighter, and when no further decrease in the colour took place the reaction mixture was poured into and thoroughly washed with water, dried in a desiccator, dissolved in acetic acid, and the solution poured into four times its volume of ether containing some light petroleum. The precipitate was washed carefully with ether, and dried over sodium hydroxide in a vacuum for 14 days, and then for one week in a high vacuum over phosphoric anhydride at 70°. The light brown powder was soluble in acetone, pyridine, alcohol and acetic acid, but insoluble in ether, light petroleum and benzene (found; C, 60·0; H, 4·1%). It was easily hydrolysed by alkali or acids, and in alkaline solutions the product absorbed oxygen with very considerable increase of colour.

Methylation of "Quinone Humic Acid."—The humic acid was prepared as in the previous experiment, and was methylated in an atmosphere of hydrogen, dimethyl sulphate (15 c.c.) and 40% sodium hydroxide (12 c.c.) being used. After repeating the process a fine suspension of the methyl derivative was obtained. Hydrochloric acid was added and the precipitate collected and washed with water. The brown amorphous powder was insoluble in alkali and ether, incompletely soluble in alcohol, and very soluble in acetone. It was dried, dissolved in acetone, the solution filtered, and precipitated with ether containing some light petroleum. The preparation was dried for analysis in the same manner as the above acetyl derivative (found: C, 63·9; H, 4·6; MeO, 23·1%).

These experiments on the composition of the amorphous products of the polymerization of benzoquinone show that the products of acid polymerization are similar to diacetoxytriphenylene dioxide, and they may contain furane groups. The products of the alkaline polymerization of quinone contain less carbon, which may perhaps indicate a lower content of furane groups. It is further noteworthy that "quinone humic acid" can easily be methylated to a product containing over 20% methoxyl. Fuchs and Leopold* methylated similar humic acids, but even after repeated methylations they obtained products containing only a small percentage of methoxyl (about 2%).

The author intends to return to this question in a later paper. The results of the methylation, however, depend very much on the method of isolation of the humic acids. In order to obtain a high degree of methylation previous intensive drying of the humic acid should be avoided.

Polymerization of Toluquinone with Sulphuric Acid.

Diacetoxytritolylene Dioxide.—A cold mixture of sulphuric acid (25 c.c.) and water (75 c.c.) was added to a vigorously shaken solution of toluquinone (10 gm.) in acetic acid (50 c.c.). The toluquinone crystallized as a fine suspension, and the shaking was continued for 3 days. The deep brown precipitate (7·7 gm.) was collected, washed with water, and dried over sulphuric acid in a vacuum. Only traces of toluquinol could be extracted by ether from the filtrate. When the dry polymerization product was added to a mixture of equal volumes of acetic anhydride and pyridine (50 c.c. in all), it rapidly dissolved, but after a minute only, a bulky colourless precipitate separated. After 15 minutes, the solid (2·5–3 gm.) was collected, and washed with acetic acid and then with methyl alcohol and ether. The crude acetate was recrystallized from paraffin and from acetic anhydride, and formed long silky needles, m.p. 285–286° (found: C, 72·0; H. 4·8. $C_{25}H_{20}O_6$ requires C, 72·1; H, 4·8%). It was sublimed in a high vacuum at 250–260°, without change either in melting point or composition. It dissolved in concentrated sulphuric acid with a deep red colour, which rapidly faded.

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* 'Brennst.-Chem.,' vol. 8, p. 73 (1927).

Dihydroxytritolylene Dioxide (I, II).—A mixture of diacetoxytritolylene dioxide (2 gm.) acetic acid (50 c.c.) and concentrated sulphuric acid (5 c.c.) was heated on the water bath in an atmosphere of hydrogen until the acetate had dissolved, and then left to cool slowly. Boiling water (200-300 c.c.) was added cautiously, and the phenol (1·6 gm.) was precipitated as a pale blue crystalline powder. A hot alcoholic solution of the phenol (charcoal) was mixed with an equal volume of warm water, and cooled; the substance crystallized and was dried immediately to avoid superficial oxidation. It formed hair-fine needles which on slow heating charred at 260–270°, but on rapid heating melted at a temperature far above 300°. The air-dried substance contained water of crystallization which was removed at 110° in a vacuum over P_2O_5 (found: H_2O, 10·4 $C_{21}H_{16}O_4$, $2H_2O$ requires H_2O, 10·3%. Found in dried material: C, 75·1; H, 5·0. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%). Neither this substance, nor any of its derivatives, reacted with hydroxylamine, phenylhydrazine, or 2 : 4-dinitrophenylhydrazine. On acetylation the original acetate was formed. This bisanhydrotritoluquinol is identical with a product obtained by Brunner,* which he supposed to have the composition $(C_7H_8O)x$.

Dimethoxytritolylene Dioxide.—An excess of dimethyl sulphate (5–10 c.c.) was added to a cold, filtered alcoholic solution (50 c.c.) of dihydroxytritolylene dioxide (2 gm.) in absence of air and followed by 40% sodium hydroxide solution (5–10 c.c. in drops). The crystalline methyl derivative soon began to separate, and after the addition of all the alkali, the reaction mixture was poured into water, and the solid collected and dried. The crude substance (2 gm.) melted at about 220°, but two recrystallizations from pyridine yielded long, thread-like needles, m.p. 232–233°. After sublimation at 250°/0·001 mm. the substance had m.p. 233–234° (found: MeO, 16·4; M (Rast in camphor) 371 : 400. $C_{21}H_{14}O_2(MeO)_2$ requires MeO, 17·2%; M, 360). The methoxyl estimation could only be accomplished as for dimethoxytriphenylene dioxide.

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* 'Mhft. Chem.,' vol. 10, p. 171 (1889).

Monobromodimethoxytritolylene Dioxide (Structure: *cf.* p. 229).—A dilute solution of bromine in chloroform was added drop by drop to a fine suspension of the methyl ether in the same solvent. The colour of the bromine disappeared almost intantly; a slight excess of bromine was added, and the mixture kept overnight. No complete decolorization had taken place, and the suspension was filtered, and the solid recrystallized thrice from pyridine and once from acetic anhydride. The monobromo derivative formed long, colourless needles, m.p. 274-275° (found: C, 62·9; H, 4·5; Br, 18·1. $C_{23}H_{19}O_4Br$ requires C, 63·0; H. 4·3; Br, 18·2%).

Mononitrodimethoxytritolylene Dioxide. (Structure: *cf.* p. 229).—A mixture of a fine suspension of dimethoxytritolylene dioxide in acetic acid and a slight excess of nitric acid (d, 1·42) was left overnight, and the long yellow needles were collected and recrystallized from pyridine or acetic anhydride. Finally, the substance was sublimed in a high vacuum at 250°. Thus purified the nitro-derivative formed a lemon yellow, highly electrified powder of small needles, m.p. 305° (found: N, 3·5. $C_{23}H_{19}O_4NO_2$ requires 3·5%).

Polymerization of α-Naphthoquinone with Sulphuric Acid.

Diacetoxytrinaphthylene Dioxide (V) and *Trinaphthobenzene Trioxide* (VI).—α-Naphthoquinone is much more stable than benzo- and toluquinone. When treated with sulphuric acid as described for these quinones, it polymerized very slowly, but a mixture of sulphuric acid and acetic acid caused rapid polymerization. The following procedure is more satisfactory.

α-Naphthoquinol (5 gm.) was dissolved in acetic acid (50 c.c.) and mixed with concentrated sulphuric acid (15 c.c.) and acetic acid (35 c.c.). α-Naphthoquinone (5 gm.) was dissolved in acetic acid (50 c.c.) and the two solutions were mixed at 40–50° and a thick grey precipitate appeared almost instantly. After cooling, the reaction mixture was poured into hot water, the solid collected, boiled with pyridine (50 c.c.) cooled, and mixed with acetic anhydride (10 c.c.). After 1 hour, the mixture was poured into water, and the precipitate (8 gm.) collected and washed with methyl alcohol, acetone, and ether. The alcohol and acetone extracts contained 1·5 gm. of amorphous substances.

In another experiment the following proportions were used: α-naphthoquinol (5 gm.) dissolved in acetic acid (50 c.c.) was mixed with a solution of sulphuric acid (15 c.c.) in acetic acid (35 c.c.) followed by α-naphthoquinone (10 gm.) in acetic acid (100 c.c.). The crude acetate weighed 14 gm. and, after being washed with acetone and methyl alcohol, 10 gm. remained. Both preparations, after the extraction of amorphous products, consisted of a pale yellow crystalline powder, part of which was soluble in a large volume of quinoline.

The quinoline-soluble portion (V) was recrystallized from paraffin in long, colourless needles. After being sublimed at 300–315°/0·0002 mm. and then boiled with acetic anhydride and washed with acetone, it melted at 340–343° (found: C, 77·4; H, 3·9. $C_{34}H_{20}O_6$ requires C, 77·9; H, 3·8%). Further sublimations did not alter the melting point or the composition. This substance exhibits a characteristic blue colour-reaction with concentrated sulphuric acid, but the colour is not stable, and soon a grey precipitate is formed. The substance is highly electrified on friction.

The quinoline-insoluble fraction (VI) (above) which formed long needles was not appreciably soluble in any of the solvents tried. It seemed to be very sparingly soluble in boiling β-naphthylamine (306°), but the only feasible method of purification has been to extract it several times with boiling quinoline, in order to remove most of the soluble substance. The last traces were sublimed away in high vacuum at 300–330°. The residue sublimed without decomposition above 400° (found after sublimation: C, 85·6; H, 2·8. $C_{30}H_{12}O_3$ requires C, 85·7; H, 2·9%). This substance did not give any colour with concentrated sulphuric acid, but dissolved (sulphonation ?) on heating. It was very stable towards cold concentrated nitric acid, but was readily attacked by fuming nitric acid. On prolonged heating to 140° with fuming nitric acid a yellow, partially crystalline, substance was obtained. When heated in the air, the compound did not melt, but charred at a temperature above 400°.

Summary.

A dihydroxytriphenylene dioxide (IV) has been isolated from the products of the polymerization of *p*-benzoquinone by sulphuric acid.

Under similar conditions toluquinone yields a dihydroxytritolylene dioxide (I, II).

Sulphuric acid converts α-naphthoquinone, alone or mixed with α-naphthoquinol into a dihydroxytrinaphthylene dioxide (V), and a neutral product, which is almost certainly trinaphthobenzene trioxide (VI).

Acknowledgements.

The investigations described in this series of papers were begun in 1925 in the laboratory of the late Professor A. Vesterberg, Stockholm.

The main part of the experimental work was carried out in the laboratories of Professor Robert Robinson, F.R.S., University College, London (1929–30), and the Dyson Perrins Laboratory, Oxford (1930–31). The author has great pleasure in acknowledging his great indebtedness to Professor Robinson for his many useful suggestions on experimental and theoretical questions, and for the laboratory facilities, which he has always most generously offered.

The author is further highly indebted to Professor F. Fichter, Basel, in whose laboratory he carried out a series of electrochemical oxidations of phenols and phenol ethers, and to Professor E. Späth, Vienna, in whose department most of the difficult purifications of the termolecular products of polymerization of quinones were achieved.

To Dr. W. Bradley, Manchester, Dr. A. Léon, Madrid, and Dr. K. N. Menon, Bangalore, the author wishes to express his gratitude for much help in connection with the laboratory work, and to Dr. J. M. Gulland, London, for his kind assistance in correcting the manuscript.

The investigations have been supported financially by a Ramsay Memorial Fellowship and by a grant from the "Liljevalch Jrs. Stipendiefond."

The Dyson Perrins Laboratory, Oxford ; Stockholm University.

Address of the President, Sir Frederick Gowland Hopkins, at the Anniversary Meeting, November 30, 1933.

Following tradition I begin by enumerating the losses our Fellowship has suffered during the year. Now that all obituary notices are to be assembled in special numbers, and will thus become easier of access, there is perhaps reason for briefer references in an Annual Address.

We have lost two of our Foreign Members and fifteen Fellows.

Emile Roux. Roux died at the age of 80 after half a century of complete devotion to science. For thirty years he was an official of the Pasteur Institute, being made Assistant when the Institute was founded in 1888, Assistant Director on the death of Pasteur in 1895, and Director in 1904. In private he lived the simplest of lives. He asked little for himself and devoted the greater part of his official salary to the support of the scientific needs of the Institute, which was often without adequate funds. He was one of Pasteur's most trusted colleagues, assisting in some of his most important researches, those upon anthrax among them. Roux's own researches and those carried out with colleagues, whom he always inspired by his unselfish devotion to the work in hand, were of fundamental importance, and form classics in the literature of bacteriology and immunology. Together with Yersin he was the first to prepare the specific toxin formed by the bacillus of diphtheria, and with Behring he was awarded a Nobel Prize for work which led to the discovery and use of anti-diphtheria serum. Roux's work as a whole covered a wide ground and represents a great contribution to medical science and to practical medicine. To the many who visited the Institute for post-graduate study he was always courteous and helpful, and he used to deliver informal lectures which were extraordinarily informative and stimulating. He was elected to our foreign membership in 1913, and received the Copley Medal in 1917.

Leon Charles Albert Calmette. After several years' experience as a ship's doctor and Colonial Medical Officer, Calmette became a member of the Medical Faculty at Lille and began there a prolonged study of tuberculosis at the local Pasteur Institute, which he himself founded. Though his scientific work covered a wide ground, his concern with tuberculosis lasted throughout his life, and his efforts were especially directed towards the discovery of an anti-tubercular serum. Ultimately this work led to the introduction of the bacillus Calmette-Guérin, for which much success in the treatment of tubercular children has been claimed in France. Its value is not yet universally accepted, but it is still under trial at several centres. Owing to severe epidemics of smallpox and many deaths from rabies in Indo-China in 1890, Calmette was sent there by Pasteur. He established a research laboratory at Saigon. He used young buffaloes for the preparation of vaccine, and instituted the Pasteur treatment against rabies. In 1893 he returned to the Pasteur Institute, Paris, where he continued his work on snake-venom begun in Saigon, producing the well-known polyvalent anti-venenin serum still employed against snake-bite. He also worked on the alcoholic fermentation of rice. In 1910 he established an Institute at Algiers. In 1917 he became sub-director of the Pasteur Institute, Paris, under his old chief and friend Professor Roux, whose death so closely followed his own. In 1920 Calmette established the Pasteur Institute in Athens. He was elected a Foreign Member of the Society in 1921.

William Cawthorne Unwin, who lived to the great age of 95, was for a long time the leading expert in engineering education. His powers, however, were not devoted alone to imparting knowledge or to applying it in practice, his endeavour was to increase it whenever he could. In his younger days especially he was devoted to research and he was apt to deplore that its importance was not sooner and more fully recognized by members of his profession. He was fortunate in being apprenticed on leaving school to Sir William Fairbairn, who inspired during the middle years of the last century much important research in engineering. After holding positions in more than one firm of engineers, in the Royal School of Naval Architecture and in the Royal Indian Engineering College, Unwin became in 1884 Professor of Civil and Mechanical Engineering in the then newly established City and Guilds Central Technical College. This position and the exceptional technical equipment of his department gave full scope and opportunities for the display of his special talents. He organized a wise and most successful course of training for his students, and many of them came to hold high positions in their profession and in industry. He acquired an international reputation and had a large practice as a consultant, and among many large enterprises in which he played a leading part was the development of Niagara as a source of power. Other more or less analogous problems were often presented to him. He resigned his Chair in 1904, but remained in touch with professional work. Though he was 77 when the war began he served throughout it on the Management Board of the Metropolitan Munitions Committee. He was elected to our Fellowship in 1886.

JOHN MILLAR THOMSON was a graduate of Glasgow University, but in 1871, when he was 22 years of age, he was appointed as a Demonstrator at King's College, and so began his long career as a teacher of chemistry in London. From 1880 to 1887 he held a Chair at Queen's College, but then returned to King's to the Daniell Chair of Chemistry, which he long occupied. His services to that institution were great and continuous, and in recognition of these the College instituted a medal associated with his name, which is awarded annually to a student distinguished in chemical studies. He was a Vice-President of the Chemical Society, and a President of the Institute of Chemistry. Most of his original investigations were concerned with technical problems, his publications dealing with the composition and properties of ancient glasses, the chemistry of building materials, and studies of putrefaction and antiseptics. He became a Fellow in 1897, and was for many years chairman of the Society's Library Committee.

HENRY REGINALD ARNULPH MALLOCK combined a great skill in mechanical construction with mathematical ability and ingenuity. He possessed a genius for direct attack on a problem; in consequence, the range of subjects with which he successfully dealt was very great. After leaving Oxford he assisted William Froude in working out the gear of the original ship model tank at Haslar; he was at one time assistant to the late Lord Rayleigh, and later Consulting Engineer to the Ordnance Board. Much of his work was confidentially undertaken on behalf of the Admiralty or War Office, and included research on ballistics and on flying. The muscles of insects' wings, the eyes of spiders, the growth of trees, the use of styrax, are among the unexpected subjects successfully investigated by him. He was made a Fellow in 1903.

ERNEST WILLIAM HOBSON, Emeritus Professor and formerly Sadleirian Professor of Pure Mathematics at Cambridge. He was Senior Wrangler in 1878. In the following year he was elected to a Fellowship at Christ's College, and for more than fifty years remained resident at Cambridge, where his familiar and striking personality will be greatly missed. He had been thirty years resident before his election to the Sadleirian Chair in 1910 gave him a position in the University proportionate to his reputation; much of his time was previously consumed in relatively elementary College teaching and coaching. The demands of such teaching led him to publish a treatise on trigonometry which was of very high merit. In 1906 appeared the first edition of what is usually held to be his *magnum opus*: "Theory of the Functions of a Real Variable." In the relative leisure provided by his Chair he brought out a greatly extended second edition of this important work. Outside pure mathematics Hobson had wide interests. He never lost touch with the general progress of science, and he read and thought much in the domain of philosophy. In 1921-22 he held the post of Gifford Lecturer in the University of Aberdeen and the book "The Domain of Natural Science," which contained the matter of his lectures, showed how widely his thought had covered the grounds of human knowledge. He became our Fellow in 1893.

VICTOR HERBERT VELEY. During his long residence at Oxford, Veley did work of great value both as an investigator and as a teacher. As a member of University College, he was one of those who by devotion to the laboratory, without neglect of College duties, strengthened the position of science in his University. He published many papers of importance in the field of inorganic chemistry, and one dealing with the "Hydrate Theory of Solution" received much attention and led to controversy when it appeared. Jointly with his wife, he investigated the behaviour of an organism isolated from Demerara rum. The organism is remarkable in that it can survive in alcohol 40° over proof. Veley was elected Fellow in 1894.

JOHN EDWARD MARR. Marr was a geologist with wide interests and great interpretive skill. His powers were especially displayed on the physiographical side of his science, and his grasp of the significance of landscape amounted to genius. His earlier work dealt with the oldest fossiliferous rocks, and a study of the life zones in those strata in the Lake District awoke a love for that part of England which never left him. He published many papers on its older rocks and on those of North-West Yorkshire. His charming and stimulating book, "The Scientific Study of Scenery," dealt largely with the Lakelands. In conjunction with Alleyne Richardson he did important work on the geology of the Cross Fell area, and made notable advances in the study of the graptolites. His joint work with Harker on the granite of Shap led to one of the earliest expositions of the more modern views on the genesis of the igneous rocks. His interest in later years turned from the most ancient to the most recent of geological periods and he devoted much time to the Pleistocene and Recent deposits of Cambridge and adjoining areas, being especially concerned with correlating the occurrence of human remains and palæolithic flint implements with the glacial events of the district. Marr had been a member of the geological staff at Cambridge for 31 years before (in 1917) he succeeded to the Woodwardian Chair. During many of those years he cheerfully bore the main burden of the Department's labours, both on the teaching and administrative side. He was a most able and stimulating teacher, alike in the field and the lecture room. His strong but ever kindly personality was loved by his pupils no less than by his colleagues. He was elected to our Fellowship in 1891, and received a Royal Medal in 1930.

OTTO STAPF was one of the leading systematic botanists of his time. After being a teacher in Vienna he was, in 1891, appointed to an Assistantship at the Royal Botanic Gardens, Kew, and officially or unofficially retained his connection with them until his death. In his younger days he travelled in Persia, and was an authority on the flora of that country, as well as on those of other Eastern lands, including India, Borneo, Malaya, and also on those of Africa. He worked intensively on several plant groups, among which were the grasses of Africa. He took much interest in the problems of geographical distribution, and was particularly concerned with the Western element in British flora. In 1922 he gave up his official connection with Kew, and became editor of Curtis's *Botanical Magazine* and of the *Index Kewensis*. The six completed volumes of the latter represent monumental labour and are of great value to all workers on systematic botany. He gave much personal help not to scientific students alone, but also to numbers of professional and amateur horticulturists. He became a Fellow of this Society in 1908.

ALFRED WILLIAM ALCOCK. It is noteworthy that this year we have lost from our Fellowship two members of the Indian Medical Service, each of whom made valuable contributions to rational knowledge. This should remind us that this Service has produced many servants of Science and in this respect should stand high in our regard. Stephenson, as I shall remind you, devoted himself more especially to an intensive study of one zoological phylum; Alcock, the older man by some twelve years—though he too as a zoologist became a recognized authority on a particular group, namely, the crustacea of India—advanced science, and in particular during his later years, when engaged in the application of zoology to tropical medicine, more by his personal enthusiasm and teaching than by his own investigations. He was a remarkable man with a remarkable career, reaching his position as Professor of Zoology in the Medical College of Bengal by very devious paths. During his tenure of that Chair amid diverse activities he organized and rearranged the Indian Museum, making it a model of its kind. From his student days at Aberdeen and throughout his life in India, he retained an intense interest in Patrick Manson's discoveries on insect-borne diseases, and on his retirement from the Indian Medical Service he came to London and gave enthusiastic services to the—then new—School of Tropical Medicine, where he taught in particular the subject of medical entomology. In 1920 he was made Professor of Medical Zoology in the University of London. Alcock was a charming and unpretentious man, immensely popular among his students and much loved by his friends. He was made a Fellow of the Royal Society in 1901.

Gilbert Charles Bourne, Emeritus Professor of Zoology and Comparative Anatomy in the University of Oxford, possessed great versatility. As an active scientific worker, as chairman of various advisory and investigating committees, as a teacher, as an oarsman and rowing coach ; in each of these and in other capacities he showed always the highest efficiency. He studied zoology under H. N. Moseley, and worked for a short time with Weismann at Freiburg. In 1885 he visited the island of Diego Garcia, a coral atoll. Then began his long-lived interest in the biology of corals, a subject to which he made important contributions. He was also interested in crustacea, and an elaborate study of Raninid crabs led him to found a new tribe—Gymnopleura. Later he was concerned with mollusca and published noteworthy papers upon them. His work as a whole forms a solid and lasting contribution to zoological science. For a short time Bourne was director of the then recently established Marine Biological Station at Plymouth. In 1906, after having taught for some years in the Oxford School of Zoology, he succeeded Weldon in the Linacre Chair, and occupied it with distinction till 1921. He was elected to the Fellowship of the Royal Society in 1910.

Leonard James Rogers long held the Chair of Mathematics at the Yorkshire College and University of Leeds. He is remarkable among our Fellows in that, according to a well-informed biographer, science was to him almost distasteful. He was, nevertheless, a brilliant mathematician, though in later life he lost interest in his own researches. Among certain propositions discovered by the famous young Indian mathematician, Ramanujan, were two that he himself and other authorities were unable to prove. A chance search through the literature led to the discovery that Rogers had stated and proved them nearly twenty years earlier. Most of his published papers dealt with the algebraical and arithmetical side of the theory of elliptic and modular functions. He was elected F.R.S. in 1924.

Sir Alexander Cruikshank Houston was for 28 years Director of Water Examinations to the Metropolitan Water Board, and was thus one of the real guardians of the health of London. While especially well qualified as a bacteriologist, he was an authority on all scientific aspects of public health service. On matters related to the maintenance of pure water supplies he was a leading authority. He graduated in Medicine at the University of Edinburgh in 1889, and after spending some time in completing his education as laboratory worker he undertook important commissions for the Local Government Board; among many others an investigation of the conditions which had led to lead poisoning by moorland water supplies. For the London County Council he engaged on sewage disposal experiments and on the bacteriology of food supplies. He was bacteriologist to the Royal Commission on Sewage Disposal which sat from 1899–1905, and in the latter year gave valuable assistance to the Corporation of Lincoln in its efforts to control a serious epidemic of typhoid fever. In 1907 he was the British representative on an international commission of three experts to enquire into the quality of the Cairo water supply, and in 1913 he went to Ottawa for a similar enquiry. Although much of Houston's original work was published in reports made to public bodies, he made important contributions to scientific progress and the researches involved were of high quality and authoritative. He published more than one important monograph on questions related to water supplies. His opinion was always greatly respected by those he worked for and by those he worked with. He was of our Fellowship for a period regrettably short, being elected in 1931.

JOHN STEPHENSON was a medical graduate of the University of Manchester, entering the Indian Medical Service in 1895. After seeing active service and holding various appointments as a Civil Surgeon, he became, in 1906, Professor of Biology in Government College, Lahore, and later Principal of that Institution. In 1920 he returned home and was appointed Lecturer in Zoology at Edinburgh. Stephenson devoted many years to the study of oligochaetes, and became an outstanding authority on that group of worms. His monograph on the subject revealed him not only as an accomplished morphologist and taxonomist, but also as one who had given much thought to the widest problems of biology. Leaving Edinburgh in 1929 he continued his investigations in London as an unofficial worker in the Natural History Museum. He devoted his leisure to the study of Persian and Arabic history and literature, and published works of interest on these subjects. He was elected to our Fellowship in 1930.

SIR WALTER FLETCHER. While Fletcher will always be remembered as the first great organizer of medical research in this country, it should not be orgotten that he was himself highly qualified as an investigator, and before he undertook the task of guiding a new national enterprise to success, he had published the results of researches of much importance to physiology and biochemistry. He was a pioneer among those who have studied by modern and adequate methods the active chemical events in muscular tissue, and his work blazed a path along which others have trod with much profit. The complete understanding of the needs of research, and the sympathy with the aspirations of the investigator which he thus acquired, constituted part of the many remarkable qualifications for the post which he came to fill with such outstanding success. Fletcher had spent twenty years in Cambridge, and was just finishing the full period of service as Tutor at Trinity College, when in 1914 he was chosen as the first Secretary of the Medical Research Committee, then newly constituted under a clause in the National Insurance Act. The war followed almost immediately, and Fletcher foreseeing, as few then foresaw, that need for research might be more urgent during war than in peace, straightway organized the resources of his Committee for the demands of the former, and ultimately earned for it the gratitude of the Service and of more than one Government Department. The Committee and its Secretary, indeed, emerged from the war with established reputations. Of the subsequent work of the Committee and of the Council which succeeded it I propose to say a few words later in this Address. The outstanding achievement of these successive bodies was founded upon the vision, genius, and loyalty of him who from the first, and for 19 years, was devoted to their service. Fletcher was elected to our Fellowship in 1915.

Among those whom we have lost during the year two were Fellows elected under Statute 12. We all know that Viscount GREY OF FALLODEN was a lover of Nature and, in spite of the heavy demands of his political career, a keen and devoted student of ornithology. His wild birds' sanctuary enabled him to make and record valuable observations on the habits of waterfowl, and many field naturalists have visited and benefited from discussions in which he would courteously engage. His book, "The Charm of Birds," published in 1927, shows how wide were his interests and how accurate his observations within the field of his choice. Lord SYDENHAM OF COMBE was a soldier and a highly distinguished public servant, always interested in the progress of science. He was an able engineer, and was on the staff of the R.I.E. College at Cooper's Hill from 1871 to 1880. He saw service in Egypt, and later held many public offices of importance. He was chairman of the Royal Commission on Contagious Diseases, and a President of the British Science Guild. Among his many publications was one upon the Principles of Graphic Statics.

The lives of the great in literature are told and retold again and again. Such books as Professor Lenard's "Great Men of Science," on the other hand, are rare. In a review of that book Lord Rutherford quotes with sympathy the following words of the author: "The study of the works of great investigators taught one that they had frequently achieved much more than they were usually given credit for. The richer the contents of their work the more of it appeared to have been forgotten in course of time by the writers of histories and text-books; or rather, the credit tended to be given to others who had later turned their attention to the subject and enlarged upon it when it was no longer new."

Yet the reputation of great builders whose work has given form to the edifice of science suffers little if there come forgetfulness of the details they have added. But he who is able to add to the structure but a stone here or there, even though it may be the keystone to an arch, may suffer the iniquity of oblivion. But the piety of the few can make up for the forgetfulness of many and those who make records for posterity should use no careless pen. That the obituary records of our Fellows should be authoritative is greatly to be desired, and I think we may claim that much care is given to them. Future historians of science cannot fail to consult them.

The Report of Council calls this year for little comment. In spite of falling rates of interest the investment of our Trust Funds remains sound and satisfactory, a circumstance due in no small degree to the watchful care of our Treasurer. For ease in dealing with these investments, when emergency arises, a small alteration in Statute 89, approved at a General Meeting of the Society, has been entered in the Statute Book by orders of Council. Generous grants have been made from the various Funds, and remaining balances are at the moment not large. During the year an addition of £9700 to the capital of the Messel Fund has been made, in fulfilment of the Will of the Testator. A sum of £2000, with part of the residue of his estate, has been bequeathed under the Will of our late Fellow, Sir Dugald Clerk, and £450 under that of Miss M. S. Gregg. The decision of Council not to appoint a successor to Professor A. Fowler on his retirement will, in the circumstances mentioned in the Report, be generally approved. Our Fellows will, I think, feel glad that the Society has been able to help the work of the Academic Assistance Council by providing office room for its work. The arrangement, however, will now shortly be terminated. Council has found satisfaction in the circumstance that a request published in last year's Report has stimulated many Fellows to present copies of their works to the Society, and hopes that the presentation of such books will continue to be regarded as a normal obligation.

The circumstance that this year has seen the deeply to be regretted close of Walter Fletcher's career of service tempts me to make reference to the work of the Medical Research Council, which in particular he served so nobly. The Royal Society should not fail to be interested in that body, since Fellows of the Society have always formed a majority of its members. This was the case when in 1910 the Council first originated, as the Medical Research Committee, and has remained true ever since. In 1920 the original Committee was by Charter converted into a Council without any real breach of continuity in its activities. The Charter, however, placed the body under a Committee of the Privy Council, a step of which the wisdom has been amply proved. In its first Annual Report the Council acknowledged that the Charter endowed it with privileges and responsibilities which before had scarcely been given to any body of scientific men, and went on to remark that "It is a further cause of gratification to the Council to know that their Charter forges a link of formal connection between the national system of medical research and the Royal Society. The Committee of the Privy Council are under the obligation of consulting the President of the Royal Society before appointing any new member of the Medical Research Council, and this must provide another wholesome avenue of influence by that free Society, which for two and a half centuries has made available for the State the best scientific advice of every generation." The consultation with your President is never omitted and it is understood that in circumstances of difficulty or uncertainty he should look to his own Council for advice. Since the original Committee began its work 24 Fellows of the Royal Society have served on it or on its successor; and they have always had the power of controlling scientific policy. I may remind you that the fund administered by the Council is relatively large and is directly derived from a parliamentary vote. In the year 1930-31 it was £148,000, though as part of national economy it was reduced to £139,000 in 1931-32. Out of this the National Institute at Hampstead with its farm laboratories at Mill Hill are supported, and likewise the scientific activities of the Industrial Health Research Board. The remaining and larger proportion of the fund is mainly distributed as research grants to individual research workers and for their expenses at Universities or at other centres in the United Kingdom. The number of individual investigators receiving financial support from the Council is of the order of 600. No one who has studied its Annual Reports and has surveyed even superficially the remarkable series—approaching 200 in number—of special reports produced by Committees or by individuals selected and supervised by the Council, can fail to be impressed by the extent and diversity of the profitable researches and by the enterprises it has supported. It is not too much to say that while 20 years ago the current contribution of this country to the scientific side of medical progress was far too small to do it honour, it is now such as to earn universal respect.

I feel that this reference to the Medical Research Council is not belated at the present time, because when it was chartered it was as part of a scheme conceived for the national organization of research which has only recently been brought to completeness by the formation, after a long delay, due in the main to political inhibitions, of the Agricultural Research Council. The yet brief activities of the latter have already shown the great importance of the work the future will provide for it. The Advisory Council of the Department of Scientific and Industrial Research with the Medical and Agricultural Research Councils collectively deal with the three main departments of man's material activities. United under the ægis of the Privy Council they are freed from the dangers of political vagaries and the inhibitions of departmental interference; the continuity of their work is secured. Moreover, careful provision has been made to secure adequate contacts within the triad of Councils, for their interests cannot fail to overlap; a nexus of responsibilities has been established. The three Secretaries are, for instance, under obligation to meet together on specific occasions for a general discussion of policy; one member at least of the Medical Council must always be on the Agricultural body, and there are other means of securing co-operation. The Charter of the Agricultural Council, like that of the Medical Council, provides that the President of the Royal Society shall be consulted before any appointment is made to its membership. Its policy and the general methods by which it is applied are very similar to those of the older body as developed by Walter Fletcher. While it delegates the consideration of special problems to advisory committees with power to co-opt suitable experts, not members of the Council, advice being thus obtained from a wide field of knowledge, it retains the essential control of an enlightened and consistent policy.

It will be easily understood that the Advisory Council of the Department of Scientific and Industrial Research has had to face problems of a kind which will trouble the Agricultural Council much less, and which has not been before the Medical Council at all. The first mentioned has had to educate its beneficiaries. The farmer to-day is much more prone to welcome scientific help than his fathers were, but when the Department of Scientific and Industrial Research began its work the industrialist was often rather suspicious and unapproachable. Since its origin in 1915 it has had slowly to encourage industry to believe in scientific research, and "to look upon it not as a last resource in difficulties but as an essential part of the business of production." In this endeavour its ideal aims have been to bring about intimate contact between industrial practice and the laboratory, to make industrial research co-operative, and to secure that so far as possible the scientific outlook should be represented not in subsidiary staffs alone, but also in positions of higher control. The Council indeed has had to learn as well as to teach; to learn the right technique for making effective contacts with industry, and to teach a gospel which 20 years ago was strange to the industrialist. Making real contacts with very diverse enterprises has involved a diversity in method; but the difficulties inherent in this circumstance have been lessened by the flexibility which has characterized the policies of the Advisory Council. That Council has indeed occasion for pride in the remarkable successes which the history of its work reveals.

A notable and, as events have shown, successful step, taken early in its history was the initiation of co-operative research associations, set up and controlled by the industries themselves with initial financial help from the Department. This policy has no exact counterpart in any other country in the world. Of these associations there are now more than twenty. The activities of the Department and its Council are now remarkably great. The relations with the research associations, the financial connection with the National Physical Laboratory, the maintenance of many research establishments of its own, the control of a large number of research boards and advisory committees, the careful administration of maintenance allowances to students in training, of senior research awards and grants for the development of special investigations; these and other activities represent a very wide field of work and influence.

This brief account of the three Councils may have covered ground familiar to many. It seems desirable, however, that the Society which was the parent of research in this country should, at right moments, be reminded of the progress of national research enterprises and register approval of policy when approval is deserved. I think all the Fellows will agree that the creation of these three Councils and the definition of their respective duties and relations has brought into being a great national research organization, to be viewed as a whole and fully worthy of the confidence of the Society and of the country. When, apart from its adequate representation on the general personnel of these bodies, the Society remembers that its ex-President, Lord Rutherford, is the Chairman of the Council which is in special touch with industry, and that its own Secretary, Sir Frank Smith, is also Secretary of that body; remembers too, that the Secretaries of the other Councils are of its Fellowship, and that its senior Secretary, Sir Henry Dale, controls (under the Medical Council) the National Institute for Medical Research; when, I say, the Royal Society remembers these circumstances, it cannot fail to feel satisfaction with its own relations with this great national enterprise. With those few who have expressed the view that the Royal Society should hold aloof from it, I myself cannot feel sympathy; such a view belongs to the past. The wisdom of some and the willing help of many have brought about a happy consummation, namely, that scientific men are now in real control of scientific policy in this country, even when it deals with enterprises endowed by the State. This consummation was foreshadowed when in 1897 the Royal Society was given charge of the National Physical Laboratory; but the assistance of the State was then but meagre and grudging; it is now more generous, though even to-day it is not fully understood by statesmen that endowment of research is among the most profitable of national investments. The final outcome of these new relations none can foretell, but current success justifies the faith that the outcome will be great.

A survey confined to our own publications alone brings conviction that the progress of research during the present year has shown all the rapidity which we are accustomed to expect. It is a matter for satisfaction that our "*A*" *Proceedings* have now become the vehicle for the publication of so large a proportion of the work done in this country on atomic physics and related subjects. Anyone who was tempted a year or so ago to believe that the atom had already yielded up its essential secrets, at least in respect of the individual entities which contribute to its structure, finds himself mistaken to-day. The electron and the proton prove to have important associates in the neutron and positron. We are now to believe that the material universe is constructed not from two only but from four fundamental unit entities. We who can only look on while such knowledge grows may wonder if the list is yet closed. We have at any rate the deuteron to consider, the nucleus of H^2.

Among the many aspects of progress in physics which tempt reference is that concerned with Cosmic Rays, so fascinating to most minds are speculations concerning their nature. It behoves me, however, to deal with matters more within my competence. Nevertheless, thinking of the more recent developments in this subject one would like to express admiration of the scientific enterprise which has taken Professor Regener many miles up into the atmosphere and deep below the surface of Lake Constance for measurements of their varying intensity; admiration no less for the similar enterprises of Compton and Kolhörster. It is interesting to learn that Regener as the result of the most recent researches by himself and his colleagues has formed the personal opinion that a part at least of cosmic radiation is electromagnetic.

It is difficult even in the briefest of references to the scientific progress of the year to ignore the claims of "heavy hydrogen" and "heavy water." We knew that there was yet something to learn concerning the molecular species present at any moment in the liquid we daily handle under all sorts of varying conditions, but to learn that so familiar a friend as water should have kept hidden from us till now so deep a secret is almost disconcerting. The recognition of the hydrogen isotope H^2 and the realization that we have been in constant contact with $H^2{}_2O$ as well as H_2O shakes our scientific complacency as forty years ago did the proof that the familiar atmosphere contained a gas till then unknown. Moreover, just as Lord Rayleigh's attention to a very small difference in the density of pure nitrogen and residual nitrogen from air led to the isolation of argon, so a small discrepancy between the chemical values for atomic weight of hydrogen and Aston's mass-spectrograph determinations (when in the latter allowance has been made for the existence of the oxygen isotopes) led Birge and Mengel to the suggestion that ordinary hydrogen might contain a heavier isotope. Once again an important discovery has followed from a firm faith in the great accuracy of modern physical measurements.

The brief history of our knowledge of heavy hydrogen assuredly illustrates the enterprise in research which is characteristic of to-day. The bare suggestion for its existence only arose in 1931, and it is scarcely more than a year since spectroscopic evidence provided by Urey and others made it sure. Yet already heavy hydrogen and heavy water have a big literature. Advances have been rapid, Lewis and Macdonald, for instance, have already prepared and studied nearly pure $H^2{}_2O$, and many of its properties have been studied by them and by others. We learn, for instance, that its freezing point is $+ 3°{\cdot}8$ C., and its boiling point $101°{\cdot}42$, that ionic mobility is in it smaller than in H_2O, and many other of its constants have been determined.

Remembering that living cells and tissues contain 70 to 80 % or more of water, and recalling its all-important biological functions, it is not surprising that much curiosity has been awakened concerning the relations of H^2_2O to life. There seems to be already evidence that when nearly pure it is unable to maintain living organisms, though we do not know at what concentration it proves, if at all, to be actually toxic. We shall want to know to what degree living cells are permeable to it, and whether they have any selective power as between H_2O and H^2_2O. It is sure that many studies to determine such points will soon be made.

The suggestion that there may arise a new organic chemistry involving a synthesis of all known types of molecule with (if it prove possible) H^1 replaced by H^2 is intriguing, but, as others have remarked, somewhat alarming. There is at any rate much more yet to be done with compounds containing H^1.

In a previous Address I have voiced the satisfaction that all concerned with the chemistry of living things must feel in the help that is now forthcoming in full measure from distinguished organic chemists towards the elucidation of the molecular constitution of such substances as vitamins and hormones, with their great biological importance. Professed biochemists are naturally making their own efforts in such directions, but they have their own problems to face in the study of events in the living plant and animal, and in that of biochemical reactions in general. The special experience and the developed intuitional skill of those whose minds are more continuously devoted to the art of synthesis cannot fail greatly to accelerate progress in this field.

I might illustrate this by several advances which have occurred during the year, but will be content with referring to the work upon vitamin C. No one acquainted with the dramatic history of scurvy in the past can fail to feel interest in the molecular constitution of a substance, the absence of which from the food involves the onset of that most serious malady. I think the history of recent dealings with this vitamin are of sufficient interest to bear recapitulation. Albert Szent-Györgyi, interested primarily in the oxido-reduction systems of animal tissues, was led, while working at Cambridge, to attempt the isolation of the substance responsible for the highly reducing properties of the adrenal cortex. He successfully obtained it from the gland in crystalline form, and afterwards separated it from orange juice. Its presence in the latter and certain of its properties made him from the first suspect that it might be related to vitamin C, but the amount available at the time was too small for successful biological tests. Szent-Györgyi then went to the United States where adrenal glands can be had in great abundance, and at the Mayo Clinic prepared the substance in relatively large amounts. On account of its acid character, strong reducing power, and colour reactions, recalling those of carbohydrate, he at first called it hexuronic acid, but later studies having shown that it did not belong to the uronic class, it now carries the name of ascorbic acid, based upon its biological properties. Szent-Györgyi, returning to his Chair at Szeged, in Hungary, soon became convinced that his substance possessed strong anti-scorbutic properties. His conviction that it was related to carbohydrate led him wisely to seek the help of Professor Haworth at Birmingham, in the determination of its constitution. The amount of material available was at first very small, but Szent-Györgyi, seeking for fresh sources of the substance, had the remarkable good fortune to find that in *paprica*, a plant very common in Hungary, and used there as a condiment, ascorbic acid is present in relatively large amounts. Adequate material for study thus at once became available. Much time has been devoted to constitutional studies in the Birmingham laboratory with conspicuous success. It is interesting to note that the methylation of hydroxyl groups, which has been of such value in carbohydrate research generally, has been also of service in this case. I must not, of course, stop to deal with the experimental steps, or the considerations which have led to the structural formula indicated by the work of Professor Haworth and his colleagues. They have shown in brief that ascorbic acid is a derivative of the hexose sugar, *l-gulose*; and that it is the lactone of a six-carbon acid with a five-membered ring. When in solution it is present as the enolic form of 3-keto-*l*-gulofuranolactone. It is right to say that certain continental workers have come to somewhat different conclusions in detail, but the evidence for the above constitution as recently presented by a group of Professor Haworth's colleagues* is very convincing. The biological evidence for the normal activity of synthetic products is not yet complete, but it seems sure that the exact nature of vitamin C cannot fail to be shortly known. To the biochemist it is of much interest to learn that a substance with such specific activity in the animal body should be a relatively simple derivative of a sugar.

I will now direct your attention to remarkable progress in another and quite different region of contact between organic chemistry and biology by saying a few words concerning work done on the pigments of flowers. The quest into the nature of these is no new one, and most will know of the brilliant researches of Richard Willstätter which carried us so far into their secrets. Yet we owe to our Fellow Professor R. Robinson highly important recent additions to our knowledge. I have chosen this field partly because the successes reached in it demonstrate impressively enough how sure is the constructive skill of the modern organic chemist, and also because it is a field in which chemistry by joining hands with cytology and genetics is giving its indispensable assistance to our understanding of the mechanisms of inheritance. Of much interest surely is the realization that the infinite variety displayed in floral coloration is based essentially on variations within one fundamental chemical scheme. By contriving a variety of different substitutions in phenolic hydroxyl groups arranged round a common central aromatic structure, Nature has provided herself with a palette which provides all that is required for her gorgeous floral colour schemes. The central structure is that of a benzo-pyrane to which a phenolic ring is attached. As you will be aware, these pigments are collectively known as anthocyanins or, when sugar residues have been removed from their several molecules, as antho*cyanidins*. For the central structure of the pigment molecule is always associated with one or more sugar molecules; the nature of the sugar varying with different pigments. Several different monoses and also bioses find a place in the molecule of one or other of these pigments. This peculiar association of carbohydrates with functional pigments is among the most striking facts of plant biochemistry. By determining the nature of the sugars and the exact position of each in the molecular architecture of individual anthocyanins, as well as by many successful new syntheses in the group, the Oxford School has greatly advanced knowledge in this interesting field. Professor Robinson has also developed a remarkable technique for the qualitative recognition of the nature of the anthocyanins present in this or that flower, and with his method he has explored the factors of pigmentation in nearly two hundred species or varieties. This technique, apart from the preliminary guidance it gives to chemical research, will prove of the greatest value to the geneticist who studies the inheritance of floral colours.

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* Herbert, Hirst, Percival, Reynolds, and Smith, 'J. Chem. Soc.,' p. 1270, September (1933).

I sometimes feel when I talk to students or read certain historical dealings with science that much exciting progress in other branches has led many at the present time to forget how great a triumph for the human intellect and for inductive science was the emergence of power to grasp the architecture of complex invisible entities, such as organic molecules, and the ability to construct them at will. I have been struck, for instance, by finding that in the book to which I have already referred, Professor Lenard has included no leading organic chemist in his list of great men of science. Since he has dealt with some of their contemporaries one feels that he should have found a place for Kekulé, Baeyer, Emil Fischer, or some other great representative of activities so notable for their fertility. His book, it should be remembered, carries as its sub-title "A History of Scientific Progress." I venture on such a comment merely by the way. No one will deny that science, and the world as a whole, owe a deep debt of gratitude to the work of organic chemists past and present. With an ulterior motive, however, I would like to say a few further words from an historical standpoint on the significance of the chemist's extraordinary success as a builder; departing somewhat from the orthodox trend of addresses such as this.

I myself, doubtless like many here, recall the intellectual atmosphere created during the later decades of the last century by the effort of teachers like Wilhelm Ostwald, Ernst Mach, and in this country by W. J. M. Rankine and Karl Pearson to free science from hypotheses, or, as it was claimed, to purge it from metaphysics. Pictorial thought about phenomena, though it might be excused by heuristic uses, must, it was urged, be *a priori* regarded as devoid of all ultimate epistemological value. It could never reach even near to actuality. The shafts of these would-be purists were specially aimed at the atomic hypothesis and in logical consequence at atomically structured molecules seriously conceived. There was, to say the truth, a little intellectual snobbery associated with this movement. I think it was Rankine who somewhere claimed that pictorial thought and the visualization of models might be left to inferior intellects; those of a higher class could dispense with such aid and proceed straightway to the kind of thought which uses differential equations. Van't Hoff by the middle 'eighties had introduced thermodynamics into chemistry to the great benefit of science; but van't Hoff never lost sight of the importance of the atomistic point of view. Ostwald, however, was urging at this time that science stood to gain by the description of all chemical phenomena without reference to atoms, and many were impressed by a view advanced by so brilliant a mind. I remember that I and certain of my companions who, while specially interested in chemistry, were engaged in medical studies about that time, being therefore divorced from mathematics, began to have doubts about our scientific salvation. It seemed as though the mental pictures evolved by a generation of organic chemists must be mere diagrams, surprisingly successful in their heuristic application, but wholly figments after all. This extreme positivist movement, however, which was really belated before it began, had scarcely gained momentum when nemesis seemed at least to overtake it. Ostwald, it has been justly said, with the intention of escaping from metaphysics, became involved in a metaphysic of his own. At any rate at the turn of the century the atom with great force seemed to declare itself to be actual.

It was at the turn of the century, too, that Miss Pockels and Lord Rayleigh initiated researches which were ultimately to yield evidence, convincing enough, for the objectivity of molecular structure as conceived by the organic chemists of the last century. For these researches, and some later observations by Hardy, led Langmuir to the study of the orientation of molecules in monomolecular films at water-air interfaces, and such studies, developed especially by N. K. Adam, have given direct information concerning the size and shape of individual parts of molecules. Such information has, of course, been extended and greatly strengthened by Bragg's X-ray studies of organic molecules. The mental constructions of the earlier organic chemists have thus proved to be no mere diagrams for heuristic use, but to a first approximation at least they represent what is actual. Where, for instance, they conceived of a carbon chain there is an actual chain; where they pictured a ring a ring is there, and the proved actuality extends to not a few details. It may fairly be said of the pictorial thought which guided the synthetic successes of the chemist that though the pictures were incomplete they were in no essentials wrong. The organic chemist has this much advantage over the atomic physicist that the actuality of the information got by disintegrating the systems he studies can be tested by reconstruction of those systems. This is, of course, the reason for the sure progress of organic chemistry, and for the practical value of its results.

Immanuel Kant you will remember, having conceived of a narrow definition of science, was disconcerted because the chemistry of his day (which he respected) did not seem to fit into it. It eluded mathematical formulation. Such hopes as he had, however, for its ultimate position among the exact sciences were based upon the existence of the atomic theory. Had he been able to foresee the coming of the power to build up organic molecules at will, he would, I think, have felt no doubt about the high claims of such accomplishments.

The history of science is falsely told, if at any time it undervalues the significance of the successes which, in the course of the last century, gave to man so great a control over matter; successes won with the aid of thought which, from the very nature of its aims, could assume no mathematical form.

Suppose, however, that under the powerful influence of leaders of thought the atomic hypothesis, and with it probably all earnest concern with the structure of molecules, had been early discredited—if, say, there had been an immediate reaction against Dalton's teaching in his own time—it is at least possible that the triumphs of organic synthesis might then have been indefinitely delayed. Chemistry would, no doubt, have developed greatly on positivist lines, for thermodynamics was fated to progress and would in any case have provided the theoretical basis for a dynamic chemistry. Yet the fertile harvests from organic synthesis might not have been in our hands to-day, for most at least who have engaged in it worked with the faith that something actual was represented in their pictorial thought. When, however, Ostwald and others were proposing to abolish the atomic and other hypotheses from the chemical field, too much of that harvest had fortunately been garnered, and its value too patent for the labourers to feel discouraged. It is clear, I think, that the histories of synthetic and physical chemistry together illustrate with special force the undeniable circumstance that the progress of any science, not only at different stages of advance, but also in respect of different aspects of that advance, calls for different modes of thought, and, therefore, that any one effective mode calls for as much respect as any other. It is, perhaps, a fortunate happening in history that the pictorial, intuitive, and, so to speak, artistic thought of the organic chemist had established itself before modern physical chemistry came to demand the mathematical mode and the attractions which go with it. The present, however, is profiting, and the future is fated to profit still more, by the union of both.

Until modern physical methods lent him their aid, the chemist's thought-models were, as he well knew, incomplete. As an architect he built successfully in many styles without knowing precisely why the bricks he used held together. The bonds he so usefully pictured had no physical meaning.

The development of the theory of electronic valency, however, has in the course of a few years carried thought surprisingly far towards an understanding of the forces which hold atoms together in organic molecules. It is only with brevity that I can refer to these advances, but I want to remind you of them, partly at least because the work of P. Debye, whom we have recently elected to our Foreign Membership, has played so distinguished a part in them. We have first to recognize the established distinction, clear if not absolute, between electrovalence and covalence. It is the form of atomic linkage denoted by the second of these terms which applies when electrons are shared by adjacent atoms, rather than transferred from one atom to the other, that is, the special, though not the sole, concern of organic chemistry. With this conception of electron-sharing as a foundation, a remarkable structure of fact and theory has arisen. The properties of the so-called covalent bond are indeed revealing themselves to ingenious experimentation with remarkable rapidity. The dimensions and strength of such bonds, and their heats of formation, have been measured by physical methods, and, moreover, by a variety of such methods, giving closely concordant results. One among the important conceptions which have emerged is that of the dipole moment. If at any locality in a molecule electrons are shared unequally by adjacent atoms, as, for various structural reasons, they often are, the molecule will be polar; the atom which has the larger share of the two binding electrons being the negative end of a bipole. The molecule as a result orientates itself in any electric field, and a measurable moment is involved. This dipole moment is one of the most fundamental characteristics of the covalent link.

The methods by which such moments are accurately measured are mainly due to Debye. It is impossible to discuss them here, but as an interesting illustration of the relatedness of physical phenomena it may be noted that the principal method depends on the determination of dielectric constants. The rationale of this will be doubtless patent to many here. Such methods, however, give the magnitude alone and not the direction of a dipole moment, but a method suggested by Sir Joseph Thomson and worked out by J. W. Williams enables the latter to be determined. I have ventured to say this much about polar factors in molecular structure because their recognition and their measurement have thrown much light on many constitutional problems, both of structure and behaviour, in the field of organic chemistry. In the elucidation of some aspects of isomerism; in determining the special configuration of the benzene ring and of condensed rings, and in aiding crucial decisions concerning the constitution of molecules like those of the oximes, azides, and other difficult cases, the recognition of polar properties has been of much service. In stereochemistry it has also greatly helped progress, and with the further all-important help of X-ray analysis this branch of structural chemistry has greatly advanced of late.

You will understand how imperfect must be my reference to the results of the modern application of physical methods in chemistry. I have chosen the elucidation of the dipole moment as a single illustration of their value. It is clear that studies of molecular structure will for the future be in the hands of the physicist no less than in those of the chemist, and that striking progress is thus assured. Aspects of the problems now arising, unlike those successfully faced at earlier stages, call for the aid of mathematical treatment. There is no suggestion, however, that pictorial thought about the organic molecule is failing in usefulness, or that modern investigators when using thought-models believe them to lack all relation with the actual.

I will now return for a few moments to experimental findings which are certainly picturable. The subject of biochemistry is likely to gain greatly from every advance that takes us further into the details of molecular structure; for in the crowded events in the living cell we may well believe that exact particularities of shape, the ability to fit with accuracy on this or that patterned surface is prominent among the factors which determine the functions and fate of the biologically active molecules. X-ray studies and studies of surface orientations are already justifying this belief. In illustration let me remind you of the interesting light which X-ray photography has thrown upon the structure of animal and vegetable fibres: silk, hairs, cellulose, and the like. Observations made by several investigators, among whom I may mention Dr. Astbury, have shown that the basal structure of such fibres consists of bundles of long chain molecules which, as molecules, can undergo reversible or irreversible stretching. In general they are formed by the polymerization of relatively simple structural units and so in X-ray photographs display periodicity along their length due to the repetition of the unit in question. I will refer to silk and hairs alone. In the former the fibres are built of extended polypeptide chains consisting, for the most part, of united residues of glycine and alanine; the unit of pattern repeating itself along the fibre axis at an interval of $2 \times 3 \cdot 5$ A. The molecular chains in silk are in the natural state already fully extended; there is no significant change in their X-ray photograph when the fibre is stretched. Hair, on the other hand, and also horn, nails, etc., are composed of the protein, α-keratin. It would appear that the polypeptide chain of the keratin molecule in hair is not extended, but is, as it were, folded on itself. The molecules become fully extended, however, when the fibre is stretched. The photograph of stretched hair becomes then analogous to that of unstretched silk. This, however, is a reversible change.

The folding of the molecule protects elements in its structure from chemical attack. The unextended chain, for instance, resists the action of steam, while the extended chain loses its power of recovery when steamed, being "set" in the extended form. [Hence the permanent wave produced by the modern hairdresser !] A point of much interest is that though all have been wrongly looked upon as composed of the same keratin, the X-ray pattern which is common to feathers and tortoiseshell is quite different from that displayed by mammalian hair. "Thus the recognized affinity between reptiles and birds and their differentiation from mammals is confirmed by the methods of molecular physics."

I will refer to but one other illustration of progress in which biochemistry has benefited from the application of physical measurements. I have referred already to the study of monomolecular films on air-water surfaces by the use of Langmuir's technique. The presence of a film changes the phase boundary potential. During the last few years Rideal and his co-workers, especially Schulman and Hughes, using a method developed from that devised by Guyot, have determined the alteration in the apparent molecular moment in a film when molecules with different polar "heads" are compared, and when the film is compressed or expanded. Upon this basis they have developed investigations dealing with chemical reactions as they occur in these two-dimensional films; obviously a study of great interest. It would seem, indeed, that the effects of the orientation of the molecules cause film reactions to differ in important respects from bulk reactions. In illustration of this I may mention a study recently published of the rate of oxidation of monolayers of unsaturated fatty acids. The striking results of this may well contribute to an understanding of oxidations in the living cell where surface phenomena are so prominent. The authors are also studying enzyme catalysis in films and the results are very suggestive.

I would like to be allowed certain remarks at this point with the frank confession that I am ill-qualified to make them.

It is clear that the great movement in atomic physics led by Heisenberg is of the positivist kind; allied at least, though far more embracing, to that which Ostwald and others hoped to bring into chemistry. The consequent tendency in physics is towards a belief that the universe is to be described in terms of mathematical relations between unimaginable entities, and some at least have not hesitated to say that in the development of modern science the pictorial faculty is proving more and more of a hindrance. Coming fresh from consideration of the successes of chemical synthesis and the modern dealings with organic molecules it is difficult to believe that this last-mentioned view has general applications. The transition from the kind of relations found between atoms in association, which seems to be so picturable, to the demand for the unimaginable in the case of the atom itself is doubtless due to circumstances which lie deep in the nature of things. We can hardly conceive, for instance, of the synthesis of an atom, however pictorial our thought about it might be. Yet to the ordinary mind the transition seems remarkably abrupt. It leaves one to wonder at any rate whether the progress of experimental studies may not yet yield for us once more an acceptable mental picture of the atom. It tempts to a speculation, in which others have indulged, as to whether the present extreme positivist tendency in theoretical physics may not be due to the ascendancy at the moment of a particular type of mind with its own particular skill and bias. With such rebellious thoughts in my own mind I was interested when reading Murphy's translation of Max Planck's fascinating book entitled "Where is Science Going?" to meet the following passage: "Indeed," writes Planck, "it is exclusively on the basis of co-operative labour and the acceptance by others of the findings of the various individual researchers that we can explain the structure of physical science as we have it to-day. That we do not construct the external world to suit our own ends, in the pursuit of science, but that *vice versa* the external world forces itself upon our recognition with its own elemental power, is a point which ought to be categorically asserted again and again in these positivistic times."

There are many who will find refreshment in the book I have quoted. In it he, who has done more than anybody to change the scientific outlook, registers afresh his protest against the tendency to deny that the principle of causation holds in nature; he discusses paths which lead from the relative to the absolute, and asserts the intellectual value of hypothesis. I use the term refreshment advisably. The positivist provides a diet for the minds of a few, but what he offers would mean starvation for those of a great many. Planck seems to provide nutriment more suited to their needs. Another book of the year I would like to mention. Not everyone can understand Eddington's "Expanding Universe" in its entirety, but all can feel its glamour. It summarizes so much that has been happening of late in what its author calls a workshop in the basement of the building of science. Among the strange products of that workshop is one that comes from the hands of Eddington himself; a Number that seems almost mystical in its properties. It is a pure number, but by its entry into equations it displays a unifying power that is truly remarkable. It would seem as though the physicist should carry the number 137 (the "fine structure constant") as an amulet. Indirectly it is concerned in justifying the claim that if you want to measure the mass of an electron a suitable procedure is to make astronomical observations of the distances and velocities of spiral nebulæ! No one reading Eddington's book, even with imperfect understanding, can fail to be impressed with the deep sense of Unity which its chapters convey; with a realization of inter-relationships among all things. The workmen in that basement workshop, of which its author speaks, may indeed be constructing foundations for the edifice of science stronger than any it has yet possessed. Are they on the other hand conspirators preparing explosives with which they hope to blow our solid, tangible and comfortable edifice up into the air? Perhaps they need watching!

Award of Medals, 1933.

The Copley Medal has been awarded to Theobald Smith, For. Mem. R.S.

Professor Theobald Smith, was Director of the Department of Animal Pathology of the Rockefeller Institute for Medical Research, Princeton, N.J., from 1914 to 1929. His researches cover the whole field of animal pathology. They have been remarkable for their originality and diversity. In 1886 with Professor Salmon he showed a new method for producing immunity from contagious diseases by inoculating with a dead bacterial vaccine killed by heat, thus advocating a principle which was re-discovered fifteen years later and has been widely used, notably for making antityphoid vaccine. In 1889 he discovered the first known instance of a disease of vertebrates transmitted by an arthropod—Texas fever of cattle due to a protozoon transmitted by a tick. He introduced differential tests for bacteria based on their biochemical action. In 1896–98 he clearly, and for the first time, distinguished between the human and bovine types of *Bacillus tuberculosis* and the forms of disease which they produce, anticipating Koch's pronouncement in 1901. In 1903 with Reagh he described the non-motile variants of certain pathogenic motile bacteria and their important serological differences. He discovered in 1904 the remarkable phenomenon known as anaphylactic shock in the guinea-pig, and his original observations, though unpublished at the time, were freely acknowledged by subsequent writers. In 1926 he discovered the very potent effect of the colostrum, the first milk of cows, in protecting calves from certain severe infections. He also made other notable original observations, such as those on the growth and toxin production of the diphtheria bacillus, and on the production of immunity by mixtures of toxin and antitoxin; he also described disease of the cow's udder communicable to man by the milk.

A Royal Medal has been awarded to Geoffrey Ingram Taylor.

Professor G. I. Taylor is distinguished for theoretical and experimental researches covering an unusually large field. In meteorology Taylor's work on turbulence in the atmosphere has very greatly advanced our knowledge, and laid the foundation of all future work on the subject. He studied the effects of turbulence on the transfer of heat and water vapour through the atmosphere and on the variation of wind with height above the ground. He investigated the formation of fog, supplementing theoretical work by his observations on S.S. "Scotia." He has also added to the knowledge of tides.

In hydrodynamics he obtained the first (and only complete) solution of a case of hydrodynamic instability in a viscous liquid, namely, when the fluid is contained between two coaxial rotating cylinders: he has discovered and explained many interesting phenomena associated with bodies moving through *rotating* liquids (in which surface effects are of minor importance); he has developed the theory of completely developed turbulence, in which statistical methods can be applied; and he has made very important advances in the theory of *compressible* fluids.

Taylor has rendered important services to metallurgy by his studies of the plastic deformation of metals, both in the form of single crystals and in the mass. In the Bakerian Lecture of 1923, in collaboration with Miss C. F. Elam, he gave the first explanation of the mechanism of distortion of single crystals of aluminium, and determined the plane on which slip occurs. In subsequent papers he extended this kinematical theory to crystals of other types. With W. S. Farren he measured the heat generated during plastic straining in crystalline aggregates like commercial copper, and with H. Quinney he has recently extended knowledge of the conditions governing the elastic breakdown and plastic distortion of such metals. This work is fundamental, and other investigators in the study of various metals have followed the same course. The plastic deformation of metals has now been studied by a number of investigators, but the foundations have been largely established on the basis of Taylor's work. Its essential feature has been the application of exact geometrical methods to the determination of the orientation of slip in metals, making use of X-ray and other measurements. Since in metals belonging to the cubic system the number of planes of possible slip is large, the problem was a difficult one.

Taylor also studied the distortion of wires passing through a draw-plate, the results of which are of great interest to the wire industry. In a recent paper he has laid foundations for a rational theory of the strength of materials—hitherto a purely empirical science.

The foregoing is merely an outline of some of Professor Taylor's work, and makes no mention of papers in which he has applied theory to problems of practical importance—*e.g.*, the determination of the torsional stiffness of air-screw blades, the design of wind-tunnels, and many other matters in which he has given inestimable assistance.

His work will remain classical in the sense that the work of Kelvin and of Rayleigh so remains, and, like those masters, his insight and his powers of analysis are keen and wide enough to grapple with problems in almost any branch of physical science so as to lead to entirely new developments.

A Royal Medal has been awarded to Patrick Playfair Laidlaw.

During a period of twenty-five years Mr. P. P. Laidlaw has made an important series of contributions to knowledge over a wide field of medical science. Throughout this time he has shown a degree of originality and a grasp of technical methods which can only be regarded as exceptional and probably without equal in any other worker in this subject at the present time.

Even in his first publication he showed this originality when he demonstrated that the stability of iron in the hæmoglobin molecule was dependent on the presence of oxygen, a fact of great significance in subsequent investigations on hæmoglobin chemistry. Following this work, he published a number of papers on the action of various drugs, and especially the natural bases, from a pharmacological aspect. Thus, he described the pharmacological action of β-indole-ethylamine; with Ewins he demonstrated the conversion of *p*-hydroxyphenylethylamine in the body to *p*-hydroxyphenyl-acetic acid, and with Dale he described the pharmacological action of histamine. The last of these experimental studies is now regarded as classical, for not only was the physiological nature of histamine shock demonstrated, but the extension of the results to surgical shock, following injury and operation in man, gave the first insight into the mechanism of this morbid condition. This led to the development of prophylactic and therapeutic methods of treating surgical shock which have been of untold benefit to mankind. In physiology also this work was revolutionary in demonstrating the part played by the capillaries in circulatory phenomena.

At a later stage Laidlaw turned his attention more particularly to the study of micro-organisms and related problems. He was the first to use spongy platinum and hydrogen in the anærobic cultivation of bacteria. With Dobell he discovered a method for growing entamœba histolytica *in vitro* and also solved the problem—one of great difficulty at the time—as to how emetine acts in curing amœbic dysentery.

With Dunkin he undertook, at the request of a public body, with funds raised in England and America for the purpose, an investigation into the cause, prevention and cure of distemper. Experimental methods of great refinement for studying this disease in ferrets and dogs were first elaborated, and from this point a means of making a non-infective vaccine which raised the immunity against the disease was discovered. Both in its scientific and practical aspects this is one of the most successful investigations in medical science.

In a recent extension of this work, in co-operation with Wilson Smith and Andrewes, he has shown that a virus can be transmitted to the ferret from cases of human infection diagnosed as influenza, and has thus discovered a technique for its further study. It has already been shown, by the use of this technique, that the serum of patients convalescing from influenza contains antibodies capable of neutralizing the virus of the animal disease, so that the investigation is one of great practical as well as scientific promise.

It is not too much to claim that Laidlaw's work on virus disease has been so successful as to introduce into this extensive field of study a spirit of great optimism.

The Davy Medal has been awarded to William Hobson Mills.

Dr. Mills is distinguished for his outstanding contributions to stereochemistry and to our knowledge of the cyanine dyes. He has made important observations in many branches of descriptive chemistry and has extended, especially, the theory of stereochemistry and strengthened its foundations by the devising and the performance of carefully planned experiments.

His work in the quinoline and benzthiazole series resulted in the preparation of novel types of photosensitizing colouring matters and this group of dyes has been classified on a more rational basis.

In the most elegant manner he has demonstrated the occurrence of molecular dissymmetry in some of the most interesting cases predicted by theory, but, prior to his work, unconfirmed in the laboratory.

By his resolution of the oxime of ketohexahydrobenzoic acid he not only justified in a new way a prediction of van't Hoff but also furnished convincing evidence of the validity of the Hantzsch-Werner theory of the configuration of the oximes.

Later he explained the existence of stereoisomerism in certain diphenyl derivatives by an "obstruction" hypothesis and he brilliantly justified his views by predicting a similar phenomenon in the naphthalene series and then demonstrating its occurrence in a suitable case.

Mills has also developed the theory and practice of spirocyclic compounds of several very different kinds, and he has added a number of elements to the list of those which, acting as a central polyvalent atom, are known to give rise to enantiomorphism.

He has made significant and characteristically ingenious contributions to the theory of the constitution of aromatic nuclei.

His researches have frequently enabled him to give a really decisive answer to a fundamental question of chemical philosophy.

The Hughes Medal has been awarded to Edward Victor Appleton.

The Heaviside layer, or reflector of electromagnetic waves in the upper atmosphere, was originally postulated to explain the bending of such waves round the earth's curvature. Appleton, in collaboration with M. A. F. Barnett, J. A. Ratcliff, and others, has brought it within the range of detailed experimental examination. Working over a moderate distance of the order of 100 kilometres, he is able to examine the interference between the direct ray, and the ray reflected from the layer, by noting the successive intensity maxima as the wave-length of the sending station is varied continuously over a small range. In this way the height of the main reflecting layer is established to be about 100 kilometres, though at night it is found to be somewhat greater. Evidence was also found of a higher reflecting layer, situated at 180 kilometres, which has come to be known as the Appleton layer.

In some of the experiments the horizontal distance was only 18 kilometres, so that the reflected ray came nearly straight down.

Appleton has shown that ionization penetrates downwards, and the height of the reflecting layer becomes less as the sun rises. During the night the number of free electrons diminishes, and the reverse process can be traced.

In a further important series of experiments Appleton and his collaborators have shown that the downcoming electric waves from the Heaviside layer are elliptically polarized in a left-handed sense. This he connected with the modification in the motion of the ions (electrons) by the earth's magnetic field, and predicted a right-hand polarization in the Southern hemisphere, a prediction since confirmed.

Mention should also be made of Appleton's earlier work (with Watson-Watt and Herd) on the wave form of atmospherics. His work as a whole is appropriately recognized by the Hughes Medal, as the methods of research are purely electrical, in the sense in which D. E. Hughes would have understood the word.

On the Stresses Induced by Flexure in a Deep Rectangular Beam.

By D. B. Smith, B.A., and R. V. Southwell, F.R.S.

(Received April 5, 1933.)

Introduction.

1. When a straight cylindrical rod is bent into a circle by couples applied at its ends, the resulting state of stress is given, with sufficient accuracy for practical purposes, by the well-known theory of St. Venant.* In that theory quantities of the second and higher orders in terms of strain are neglected, and the resulting solution asserts that the stress is purely longitudinal, so that the rod may be thought of as an assembly of cylindrical fibres, each of which behaves independently of its neighbours.

It is evident that this description cannot be exact; for a fibre bent into a circle cannot be kept in tension unless radial forces operate to maintain equilibrium, and in the case considered such forces can come only from actions between adjacent fibres. The apparent paradox is explained by the consideration that those actions are of the second order in terms of the curvature, and accordingly are neglected in St. Venant's theory. In connection with a certain problem of elastic instability it was thought desirable to attempt a more accurate description for a particular case, namely, a rod of deep and thin rectangular section. It was found that the equations of equilibrium can be integrated independently of any simplifying assumption, and the stress-distribution determined for curvature of any magnitude. The results have no great practical importance, since they show that St. Venant's theory gives a close approximation to the facts within that range of strains which actual materials can sustain elastically; but they have some theoretical interest, and accordingly are presented in this paper.

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* Frequently described as the "Bernouilli-Euler Theory." But (*cf.* A. E. H. Love, 'Mathematical Theory of Elasticity,' Historical Introduction and § 87) in Bernouilli's and Euler's work on the *elastica* the rod is, in effect, thought of as a line of particles which resists bending; the resistance is assumed to arise from the extension and contraction of longitudinal filaments, but the precise nature of the state of stress is not investigated. Coulomb considered the flexure of beams of finite section, and determined the position of the neutral axis; but his theory still retains the two contradictory assumptions, (1) that the strain consists solely of extensions and contractions of longitudinal filaments, and (2) that the stress is purely longitudinal. It was left for St. Venant (in his memoir of 1855 on torsion) to resolve the discrepancy by showing that the stress is purely longitudinal and as such involves (in addition to extensions and contractions of longitudinal filaments) lateral contractions and extensions which have the effect of distorting longitudinal sections, perpendicular to the plane of bending, into anticlastic surfaces. It has therefore seemed to us that the exact solution for uniform flexure should be attributed to St. Venant.

Formulation of the Governing Equations.

2. The thickness t of the rod (or plate) is assumed to be so small in relation to its depth d in the plane of bending that the stresses can be neglected on planes which are parallel to this plane. In other words, we postulate a state of "plane stress."*

We imagine the plate to be bent into a circular form, and its ends to be cemented together. Evidently, in the state of stress which results when the external forces are removed, every section of the plate through the axis of curvature (C, fig. 1), will be similarly stressed, and any line which in the unstrained configuration lay along the length of the plate will be bent into a circle. Further, there can (by symmetry) be no shear stress on plane sections which contain the axis of curvature, and the normal stresses on those sections must, in order to provide the resistance to bending, pass from positive (tensile) values at the outer edge to negative (compressive) values at the inner. Somewhere on the section (but not necessarily on the central line, as in St. Venant's solution) the longitudinal strain must be zero; we take it to be zero at points distant R from the centre of curvature, *i.e.* at points on the circle NN in fig. 1.

3. Considering the unstrained configuration, let the distance from NN of a point P be y, taken positive when P lies on the side which in the strained state is subjected to tension. We do not know the position of NN in relation to the edges; but if we define the "tension edge" by

and the "compression edge" by
$$\left.\begin{aligned} y &= d_1 \\ -y &= d_2 \end{aligned}\right\} \qquad (1)$$

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* Love, 'Mathematical Theory of Elasticity,' §§ 51, 94.

we have

$$d_1 + d_2 = d, \tag{2}$$

where d is the depth of the plate.

In the strained configuration P will in general lie at a different distance from NN. Denoting this distance by $y + u$ (where u is a function of y), we see from fig. 1 that P will lie at a distance r from the centre of curvature, where

$$r = \mathrm{R} + y + u. \tag{3}$$

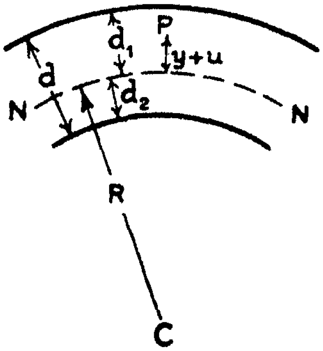

FIG. 1.

Using the symbols e_r, e_l to denote the radial and longitudinal (or circumferential) stretches, we see from the figure that

$$\left.\begin{aligned} e_r &= \frac{dr}{dy} - 1 = \frac{du}{dy}, \\ e_l &= \frac{r}{\mathrm{R}} - 1 = \frac{y+u}{\mathrm{R}}, \end{aligned}\right\} \tag{4}$$

and hence we have

$$e_r = \frac{d}{dy}(\mathrm{R}e_l - y) = \mathrm{R}\frac{de_l}{dy} - 1. \tag{5}$$

4. It follows from what has been written that e_r, e_l are principal strains at the point P. Let p_r, p_l stand for the corresponding principal stresses (radial and longitudinal); the third stress is zero on our assumption of conditions of plane stress. We must now make some assumption, relating p_r, p_l with e_r, e_l, which will be applicable when (as is here contemplated) the strains are so large that their squares and products are no longer to be neglected. The theory of finite strains is a problem in kinematics which has been fully worked out*; but in the nature of the case it affords no indication regarding stress-

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* *Cf*, Love, *op. cit.*, Appendix to Chap. I.

strain relations, and appeal to experiment is not possible, since in these only small strains are permissible. Our choice must accordingly be arbitrary, and we shall adopt the standpoint taken by one of us in an earlier paper concerned with finite strains.*

It may be shown that in any distortion, however great, three orthogonal linear elements issue from any point, after distortion, which were also orthogonal in the unstrained configuration;† hence an elementary parallelopiped constructed at the point, with sides parallel to these linear elements, will undergo no change of angle in the distortion. If the material is isotropic, it is clear that only normal stresses will act upon its faces after distortion; and if these normal stresses are expressed in terms of the extensions of its sides we have complete relations between stress and strain. We assume that the principal stresses and principal extensions, whatever their magnitude, are related by the ordinary equations (Hooke's law); and for this purpose we take as the measure of stress

$$\frac{\text{total action over an element of surface}}{\text{area of the element } \textit{before} \text{ strain}},$$

and as the measure of the extension

$$\frac{\text{increase in length of linear element}}{\text{length of the element } \textit{before} \text{ strain}}.$$

The validity of the following analysis is, of course, dependent on these assumptions.

On this understanding, p_r, p_l are related with e_r, e_l by the equations

$$\left.\begin{aligned} p_r &= \frac{E}{1-\sigma^2}(e_r + \sigma e_l), \\ p_l &= \frac{E}{1-\sigma^2}(e_l + \sigma e_r), \end{aligned}\right\} \tag{6}$$

where E is Young's Modulus and σ is Poisson's Ratio for the material composing the plate.

5. The condition for equilibrium in the radial direction is

$$\frac{d}{dr}(rp_r) = p_l. \tag{7}$$

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* Southwell, 'Phil. Trans.,' A, vol. 213, pp. 192–3 (1913).

† Love, *loc. cit.*, § 27.

Substituting from (6) we have

$$\frac{d}{dr}\{r(e_r + \sigma e_l)\} = e_l + \sigma e_r, \tag{8}$$

and from (3) and (4) we have

$$\frac{dr}{dy} = 1 + \frac{du}{dy} = 1 + e_r.$$

Hence we may write

$$\frac{d}{dr} \equiv \frac{1}{1 + e_r}\frac{d}{dy}.$$

Also we have, from the second of (4),

$$r = \mathrm{R}(1 + e_l).$$

Making these substitutions, we can replace (8) by the equation

$$\frac{1}{1 + e_r}\frac{d}{dy}\{\mathrm{R}(1 + e_l)(e_r + \sigma e_l)\} = e_l + \sigma e_r, \tag{9}$$

and finally, if we substitute for e_r from (5), we obtain a differential equation in e_l only, which (after simplification) can be put into the form

$$\frac{d}{dy}\left(\mathrm{R}\frac{de_l}{dy} + \sigma e_l\right) = (1 - \sigma)\frac{de_l}{dy}\left(1 - \frac{\mathrm{R}}{1 + e_l}\frac{de_l}{dy}\right). \tag{10}$$

Solution of the Governing Equation.

6. For convenience we now write Z for e_l and x for y/R. Then (10) can be written in the form

$$Z'' - (1 - 2\sigma)Z' + (1 - \sigma)\frac{Z'^2}{1 + Z} = 0,$$

where dashes denote differentiations with respect to x.

Dividing by Z′, and integrating the resulting equation, we obtain

$$\log Z' + (1 - \sigma)\log(1 + Z) = (1 - 2\sigma)x + \text{const.}$$

or

$$Z'(1 + Z)^{1-\sigma} = \mathrm{A}e^{(1-2\sigma)x},$$

where A is a constant of integration ; and this equation again can be integrated in the form

$$(1 + Z)^{2-\sigma} = \mathrm{B}e^{(1-2\sigma)x} + \mathrm{C}, \tag{11}$$

where B and C are constants of integration.

Now the origin has been chosen so that Z ($= e_l$) vanishes with y,—*i.e.* with x. So we have $\mathrm{B} + \mathrm{C} = 1$, and hence

$$(1 + e_l)^{2-\sigma} = 1 + \mathrm{B}\{e^{(1-2\sigma)x} - 1\}, \tag{12}$$

where B is arbitrary. Then from (5) we have

$$\begin{aligned} e_r &= \frac{de_l}{dx} - 1, \\ &= -1 + \frac{1-2\sigma}{2-\sigma}\,\mathrm{B}e^{(1-2\sigma)x}[1 + \mathrm{B}\{e^{(1-2\sigma)x} - 1\}]^{-\frac{1-\sigma}{2-\sigma}}, \end{aligned} \tag{13}$$

as the corresponding expression for the radial strain. In (12) and (13), x stands for the ratio y/R.

7. If (for brevity) we now write

$$\mathrm{F}(x) = [1 + \mathrm{B}\{e^{(1-2\sigma)x} - 1\}]^{\frac{1}{2-\sigma}}, \tag{14}$$

we have from (6), as expressions for the principal stresses,

$$\left.\begin{aligned} (1-\sigma^2)\frac{p_r}{\mathrm{E}} &= e_r + \sigma e_l, \\ &= -(1+\sigma) + \sigma\mathrm{F}(x) + \frac{1-2\sigma}{2-\sigma}\,\mathrm{B}e^{(1-2\sigma)x}\{\mathrm{F}(x)\}^{-(1-\sigma)}, \\ (1-\sigma^2)\frac{p_l}{\mathrm{E}} &= e_l + \sigma e_r, \\ &= -(1+\sigma) + \mathrm{F}(x) + \sigma\,\frac{1-2\sigma}{2-\sigma}\,\mathrm{B}e^{(1-2\sigma)x}\{\mathrm{F}(x)\}^{-(1-\sigma)}, \end{aligned}\right\} \tag{15}$$

when we substitute for e_r, e_l from (12) and (13).

Now p_r must vanish when $y = d_1$ or $-d_2$,—*i.e.* when

$$\left.\begin{aligned} & x = x_1 = \frac{d_1}{\mathrm{R}} \\ \text{and when}\quad & \\ & x = x_2 = -\frac{d_2}{\mathrm{R}}. \end{aligned}\right\} \tag{16}$$

Hence, assuming a value for B, and determining positive and negative values x_1, x_2 at which the expression (15) for p_r is zero, we can deduce the corresponding values of d/R from the expression

$$\frac{d}{\mathrm{R}} = \frac{d_1 + d_2}{\mathrm{R}} = x_1 - x_2. \tag{17}$$

Also (B having been assumed) the expressions (15) for p_r and p_l will be definite. Thus a complete solution will be obtained.

St. Venant's Solution regarded as a Special Case.

8. In St. Venant's solution the stress distribution is obtained on the assumption that d/R is very small, so that terms of order x^2 (in our notation) can be neglected in comparison with terms of order x.

Now if in (14) and (15) we treat x as a small quantity whose square can be neglected, we have

$$\left.\begin{aligned} \mathrm{F}(x) &= [1+\mathrm{B}(1-2\sigma)x]^{\frac{1}{2-\sigma}} \\ &= 1+\mathrm{A}x, \\ [\mathrm{F}(x)]^{-(1-\sigma)} &= [1+\mathrm{A}x]^{-(1-\sigma)} \\ &= 1-(1-\sigma)\mathrm{A}x, \\ e^{(1-2\sigma)x} &= 1+(1-2\sigma)x, \end{aligned}\right\} \qquad (18)$$

where A is written* for $\dfrac{1-2\sigma}{2-\sigma}\mathrm{B}$.

Accordingly the expressions (15) reduce on this understanding to

$$\left.\begin{aligned} (1-\sigma^2)\frac{p_r}{\mathrm{E}} &= (\mathrm{A}-1)\{1-(1-\sigma)\mathrm{A}x\}, \\ (1-\sigma^2)\frac{p_l}{\mathrm{E}} &= \sigma(\mathrm{A}-1)+(1-\sigma)\mathrm{A}x(1+2\sigma-\sigma\mathrm{A}), \end{aligned}\right\} \qquad (19)$$

and in order that p_r may vanish both when $x = x_1$ and when $x = x_2$ we must have

$$\left.\begin{aligned} &\mathrm{A} = 1, \\ \text{so that}\quad &p_r = 0, \qquad p_l = \mathrm{E}x = \mathrm{E}\frac{y}{\mathrm{R}}. \end{aligned}\right\} \qquad (20)$$

This is St. Venant's solution.

Numerical Solution of the Governing Equations.†

9. Reverting to the general case of our problem (§ 7), we replace B by $\mathrm{A}\left(=\dfrac{1-2\sigma}{2-\sigma}\mathrm{B}\right)$ in the first of (15), and thus obtain as the condition for a zero value of p_r

$$\left.\begin{aligned} 1+\sigma = \sigma\left[1+\frac{2-\sigma}{1-2\sigma}\mathrm{A}(\eta-1)\right]^{\frac{1}{2-\sigma}} \\ +\mathrm{A}\eta\left[1+\frac{2-\sigma}{1-2\sigma}\mathrm{A}(\eta-1)\right]^{-\frac{1-\sigma}{2-\sigma}} \\ = \Delta \text{ (say)}, \end{aligned}\right\} \qquad (21)$$

where η is written for $e^{(1-2\sigma)x}$.

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* In § 6 the symbol A was employed in a different significance; but that significance will not be required again.

† A graphical treatment of equation (21) is described in § 13.

Solutions must be sought by numerical methods, and for this purpose it is necessary to assume a value for σ. We take the value 0·3 as representative of steel, and accordingly replace the condition (21) by

$$1\cdot 3 = \Delta = 0\cdot 3\left[1 + \frac{1\cdot 7}{0\cdot 4}\mathrm{A}(\eta - 1)\right]^{1/1\cdot 7} + \mathrm{A}\eta\left[1 + \frac{1\cdot 7}{0\cdot 4}\mathrm{A}(\eta - 1)\right]^{-0\cdot 7/1\cdot 7}. \quad (22)$$

We see from the solution just obtained that reasonably small values of x_1 and x_2 (the values of x for which p_r vanishes) may be expected to correspond with values of A in the neighbourhood of unity; and actual trial has shown that the value $\mathrm{A} = 0\cdot 9$ corresponds with a value for

$$\frac{d}{\mathrm{R}} = x_1 - x_2 \quad (17)\,bis$$

of the order of 0·6. This value of d/R would entail longitudinal stresses ranging from positive to negative through a total range of about 0·6 E, and accordingly having intensities which are quite outside the power of actual materials to sustain. If (as sufficient for any practical application) we confine our attention to the range

$$0 < \frac{d}{\mathrm{R}} < 0\cdot 1, \quad (23)$$

we shall be concerned with values of A lying between 0·99 and unity.

10. In fig. 2 curves are plotted to exhibit the relation of Δ to x for a number of constant values of A; the values of Δ which have been calculated for this purpose are indicated by circles on the curves. Each curve intersects the line $\Delta = 1\cdot 3$ in two points which fix the values of x_1 and x_2 in (16); their distance apart, by (17), fixes the value of d/R to which the curve relates. Between these points of intersection Δ has values less than 1·3; the difference

$$1\cdot 3 - \Delta = -(1 - \sigma^2)\frac{p_r}{\mathrm{E}} \text{ by the first of (15),}$$

$$= -0\cdot 91\frac{p_r}{\mathrm{E}} \text{ (since the value of 0·3 has been assigned to } \sigma\text{)}, \quad (24)$$

gives the magnitude of p_r at the corresponding point in the cross-section. It will be seen that this stress is compressive, as we should expect. When $\mathrm{A} = 0\cdot 995$ ($d/\mathrm{R} = 0\cdot 21$ approximately) its magnitude is about 0·0055 E (about 75 tons per square inch for steel). In practice, curvature of this magnitude could not, of course, be sustained elastically.

It will also be seen from the figures that the neutral axis ($x = 0$) lies very approximately half-way between the inner and outer edges, even when the curvature is considerable. There is, however, a perceptible displacement towards the compression side.

Fig. 3 exhibits curves of the same kind as fig. 2, but relating to a narrower range of values for A, and plotted on a more open scale. Their interpretation is similar.

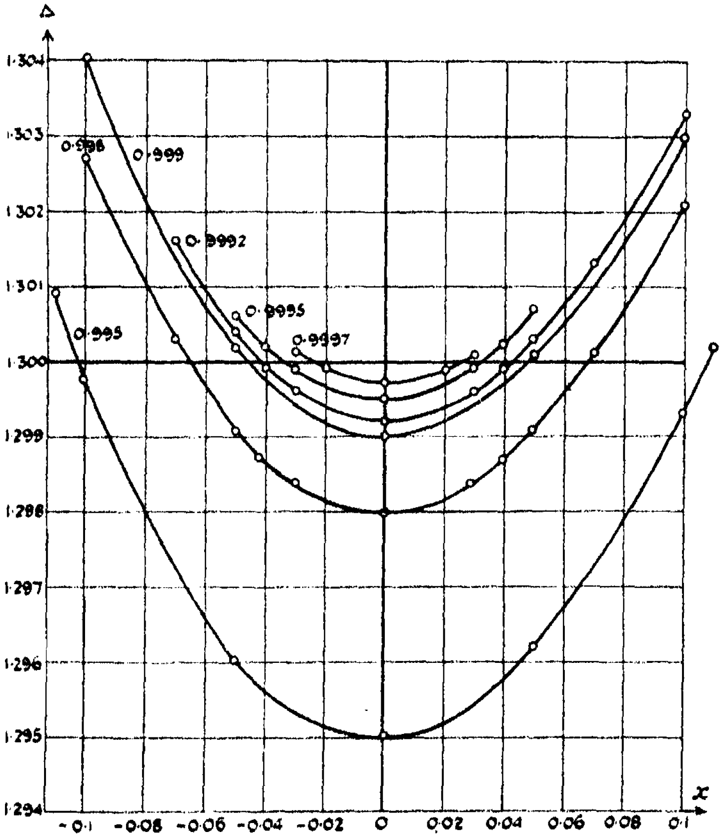

Fig. 2.—Curves relating Δ and x. (The numbers attached to the curves give the corresponding values of A.)

Approximate Solutions.

11. From figs. 2 and 3 values of d/R have been determined for a series of values of A, and the relation between A and d/R, as thus found, is shown in fig. 4. Points obtained in the manner here described are indicated in the diagram by crosses; the full-line curve drawn through them can be used to fix the value of A,—*i.e.* of B in the expressions (15) for the stress components. The significance of the circles will appear later.

We see that the relation is approximately parabolic. This conclusion (for small values of x) is also indicated by the investigation of § 8, since we there found that $(A - 1)$ vanishes when the second and higher powers of x are neglected. It suggests an examination of the expression for p_r on the basis that the third and higher powers of x are to be neglected and A is to be replaced by $1 - \lambda$, where λ is a small quantity of order x^2 at least.

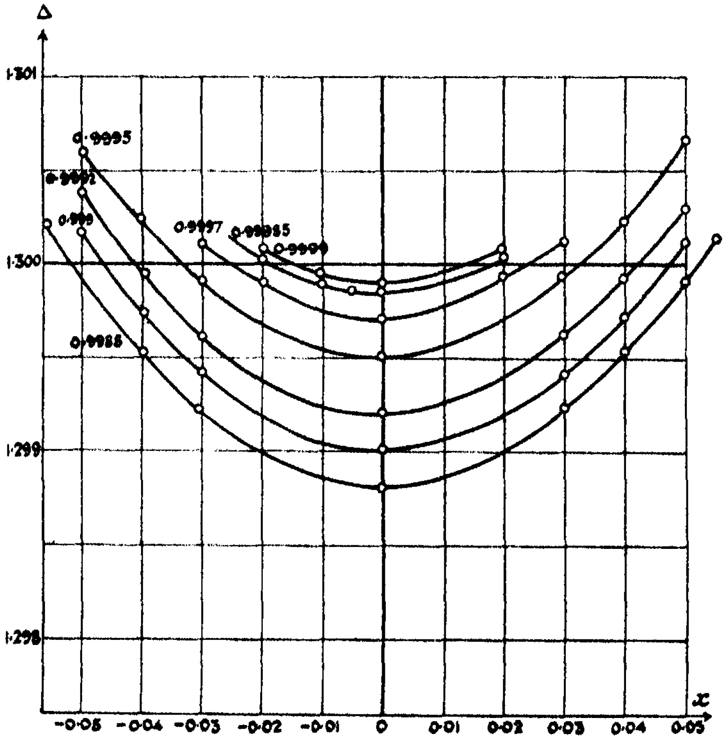

FIG. 3.—Curves relating Δ to x. (The numbers attached to the curves give the corresponding values of A.)

On this understanding we have from (14)

$$F(x) = 1 + \frac{A}{1 - 2\sigma}\{e^{(1-2\sigma)x} - 1\} - \frac{1 - \sigma}{2}\,\frac{A^2}{(1 - 2\sigma)^2}\{e^{(1-2\sigma)x} - 1\}^2 \dots$$

$$= 1 + A\left\{x + \frac{1 - 2\sigma}{2}x^2 \dots\right\} - \frac{1 - \sigma}{2}A^2x^2 \dots$$

$$= 1 + x - \frac{\sigma}{2}x^2 \dots,$$

so that

$$[\mathrm{F}(x)]^{-(1-\sigma)} = 1-(1-\sigma)\left(x-\frac{\sigma}{2}x^2\ldots\right)+\frac{(1-\sigma)(2-\sigma)}{2}(x^2\ldots)\ldots$$

$$= 1-(1-\sigma)x+(1-\sigma)x^2\ldots,$$

and

$$\mathrm{A}e^{(1-2\sigma)x} = 1-\lambda+(1-2\sigma)x+\frac{(1-2\sigma)^2}{2}x^2\ldots.$$

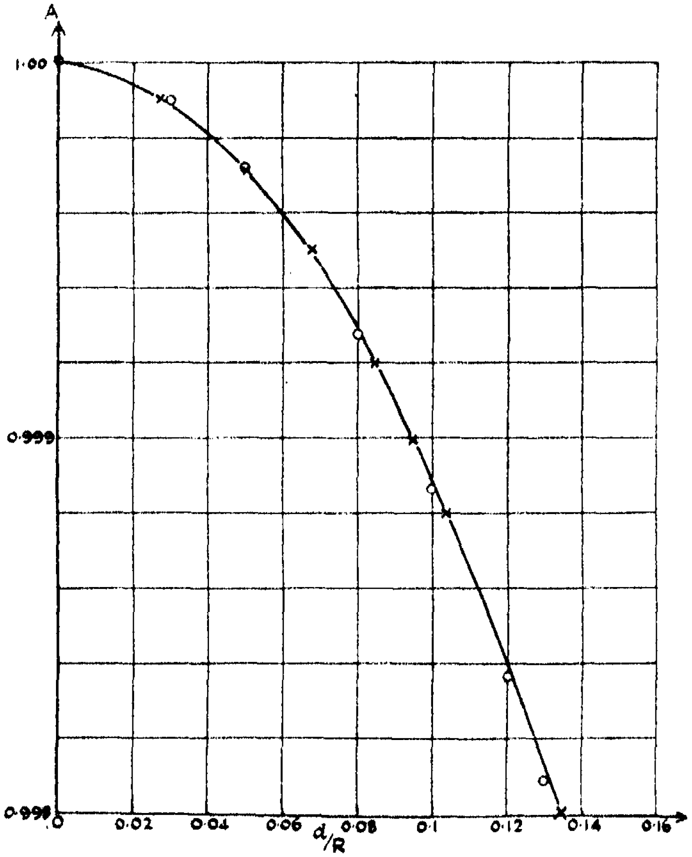

Fig. 4.—× "exact" values obtained by cross-plotting; ○ values calculated from the approximate formula (26).

Substituting in the first of (15), we have (to the same approximation) the expression

$$(1-\sigma^2)\frac{p_r}{\mathrm{E}} = -\lambda+\frac{1-\sigma^2}{2}x^2\ldots, \tag{25}$$

which gives as the values of x for which p_r vanishes

$$x_1,\ x_2 = \pm\sqrt{\left(\frac{2\lambda}{1-\sigma^2}\right)}.$$

According to this solution we shall have

$$\frac{d}{R} = 2\sqrt{\left(\frac{2\lambda}{1-\sigma^2}\right)},$$

whence

$$A = 1 - \lambda = 1 - \frac{1-\sigma^2}{8}\left(\frac{d}{R}\right)^2, \tag{26}$$

is the corresponding approximation to the value of A.

12. In fig. 4, the relation of A to d/R, according to (26), is indicated by circles.* The close agreement indicates that for practical purposes it is not necessary to proceed to a third approximation, although this could be obtained without difficulty if desired.

According to the second approximation, the neutral axis is midway between the free edges of the strip. We have from (25) and (26)

$$\frac{p_r}{E} = \frac{1}{8}\frac{4y^2 - d^2}{R^2}, \tag{27}$$

and from the second of (15), as the corresponding approximation to p_t,

$$\frac{p_t}{E} = \frac{y}{R} - \frac{\sigma}{8}\left(\frac{d}{R}\right)^2. \tag{28}$$

This constitutes a second approximation to the stress distribution involved in uniform flexure of a deep rectangular strip, and it reduces to St. Venant's solution when terms of order $(d/R)^2$ are neglected. It should be observed that p_r and p_t, as given by (27) and (28), do not satisfy (7) when terms of this order are retained: the reason is that terms of order $(y/R)^3$, in p_r, will (on this basis) contribute to the expression on the left-hand side of that equation.

13. (*Added September* 30, 1933).—As an alternative to numerical treatment of (21), Professor L. N. G. Filon has suggested the ingenious graphical method which follows. We are indebted to him for permission to include it here.

Writing

$$1 + \frac{2-\sigma}{1-2\sigma}A(\eta - 1) = \xi^{2-\sigma}, \tag{i}$$

we have from (21)

$$\begin{aligned} 1 + \sigma &= \sigma\xi + A\eta\xi^{\sigma-1} \\ &= \frac{1-\sigma^2}{2-\sigma}\xi + \left(A - \frac{1-2\sigma}{2-\sigma}\right)\xi^{\sigma-1}, \end{aligned} \tag{ii}$$

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* The relation (26), being parabolic, might have been represented in this diagram by a continuous curve; but since this would lie very close to the full-line curve (which has been drawn to pass through the crosses), representation by a series of *points* has been thought preferable.

by (i) again. This relation may be written in the form

$$\left.\begin{aligned} \xi^{\sigma-1} &= \mathrm{C}\left(\frac{2-\sigma}{1-\sigma}-\xi\right), \\ \text{where} \qquad \mathrm{C} &= (1-\sigma^2)/\{(2-\sigma)\,\mathrm{A}-(1-2\sigma)\}, \end{aligned}\right\} \qquad \text{(iii)}$$

and hence we see that the required values of ξ will be given by the points of intersection, in a (ξ, ζ) diagram, of the curve

$$\zeta = \xi^{\sigma-1} \qquad \text{(iv)}$$

(which can be constructed once for all) and of the straight line

$$\zeta = \mathrm{C}\left(\frac{2-\sigma}{1-\sigma}-\xi\right), \qquad \text{(v)}$$

which passes through a fixed point K $\left(\xi = \dfrac{2-\sigma}{1-\sigma}\right)$ on the axis $(\zeta = 0)$.

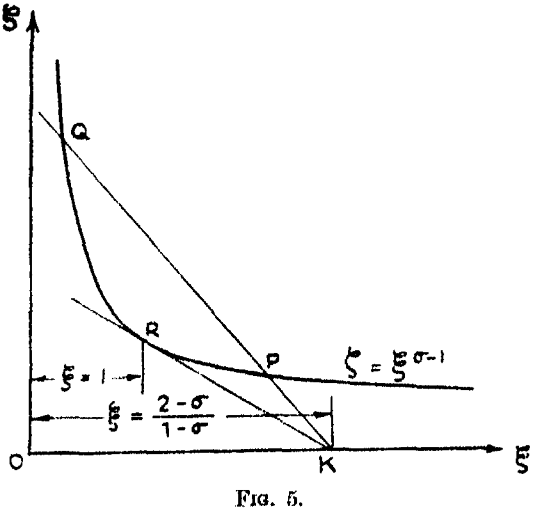

FIG. 5.

Referring to fig. 5, we see that there will be in general two points of intersection P, Q, giving two real values ξ_1, ξ_2 from which x_1, x_2 may be calculated with the use of (i). The points of intersection coincide as shown at R (so that $x_1 = x_2$, and the depth of the beam vanishes) if C is so chosen that (v) is tangential to (iv); that is, if

$$(1-\sigma)\,\xi_1^{\sigma-2} = \mathrm{C} = (1-\sigma)\,\xi_1^{\sigma-1}/\{2-\sigma-(1-\sigma)\,\xi_1\},$$

or if

$$\xi_1 = 1, \qquad \mathrm{C} = 1-\sigma,$$

so that

$$A = 1$$

by the second of (iii). This is the limiting case treated in § 8.

In the general case we have

$$\eta_1/\eta_2 = e^{(1-2\sigma)(x_1-x_2)} = e^{(1-2\sigma)d/R}, \text{ by (17)},$$

$$= k \text{ (say)}, \qquad \text{(vi)}$$

and from (ii) and (iii)

$$A\eta C\left(\frac{2-\sigma}{1-\sigma} - \xi\right) = 1 + \sigma - \sigma\xi.$$

Therefore

$$k\{2 - \sigma - (1-\sigma)\xi_1\}(1 + \sigma - \sigma\xi_2)$$

$$= \{2 - \sigma - (1-\sigma)\xi_2\}(1 + \sigma - \sigma\xi_1), \qquad \text{(vii)}$$

so that, given k (which is known when d/R is specified), we can draw a rectangular hyperbola to relate ξ_1, ξ_2. Also by means of the diagram sketched in fig. 5 we can relate ξ_1, ξ_2 by a curve which involves no parameter other than σ. Hence the problem can be solved directly, once this curve is drawn, by finding its points of intersection with the appropriate rectangular hyperbola.

Summary.

In St. Venant's well-known solution of the problem of flexure, terminal couples applied to a cylinder of isotropic material induce stresses which are purely longitudinal. It is evident that this solution cannot be exact, because radial forces are required to maintain tension or compression in a longitudinal fibre which is bent into a circular arc. The explanation of the apparent paradox is that these radial forces are of the second order in terms of the curvature, and as such are neglected in St. Venant's approximation.

Regarded as an example of "plane stress," the special case of a thin flat strip bent in its own plane can be treated by exact methods which involve no simplifying assumption, and the resulting equations are integrable. St. Venant's solution results as a first approximation, when quantities of the second order in terms of curvature are neglected; and the second approximation (neglecting quantities of the third order) agrees very closely with the exact solution throughout the range of curvatures which could be realized in actual materials without impairing their elasticity.

The Valve Maintained Tuning Fork as a Primary Standard of Frequency.

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(Communicated by Sir Joseph Petavel, F.R.S.—Received July 28, 1933.)

Introduction.

In 1922 an investigation* was carried out at the National Physical Laboratory to determine the constancy of frequency that could be expected from a valve maintained tuning fork. It was found that the fork was capable of operating with a degree of steadiness of frequency which was greater than was then necessary for most purposes. The investigation resulted in the design of a 1000 cycles per second fork which served as the Laboratory frequency standard until 1931. For precision work it was necessary to measure the frequency of the fork during the observations by comparison with a standard Shortt clock; but if the accuracy required was less than 2 parts in 10^5 it was sufficient to apply a correction for temperature to the nominal value of the fork frequency.

With the rapid advance in radio frequency technique and the ever-increasing number of wireless transmitting stations the problem of frequency standardization became increasingly important; and it was decided to instal a standard, which should be in continuous operation at a frequency within 1 part in 10^6 of its nominal value. As the most suitable frequency for use in conjunction with the existing equipment for the measurement of radio frequencies was 1000 cycles per second, and as the tuning fork had hitherto given a satisfactory performance, it was decided to continue the investigations on the fork to determine whether it could form a frequency standard of the desired degree of accuracy.

General Design of the Fork Unit.

In order that the following experiments may be clearly understood, a brief description of the fork unit will be given. The term fork unit is used to denote the complete assembly of the fork, bar magnets and coils as shown in fig. 1*a*. The fork proper, marked A, is cut from a bar of "elinvar" steel. It is clamped between the mild steel clamps B, which fit closely round the base of the fork. The magnet steel bars C are bolted into the same clamps and are separated at the top of the unit by a brass bar D. The ebonite bobbins E and F fit tightly on to the cores, which consist of No. 26 S.W.G. iron wire, packed into holes in the magnets. The grid coil is wound on bobbin F. It consists of about 12,000 turns of No. 47 S.W.G. single silk covered copper wire. There are two windings on bobbin E. The anode winding consists of 9000 turns of No. 47 S.W.G. silk covered copper wire. Beneath this is an output winding of 2000 turns of No. 42 S.W.G. silk covered wire.

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* Dye, 'Proc. Roy. Soc.,' A, vol. 103, p. 240 (1923).

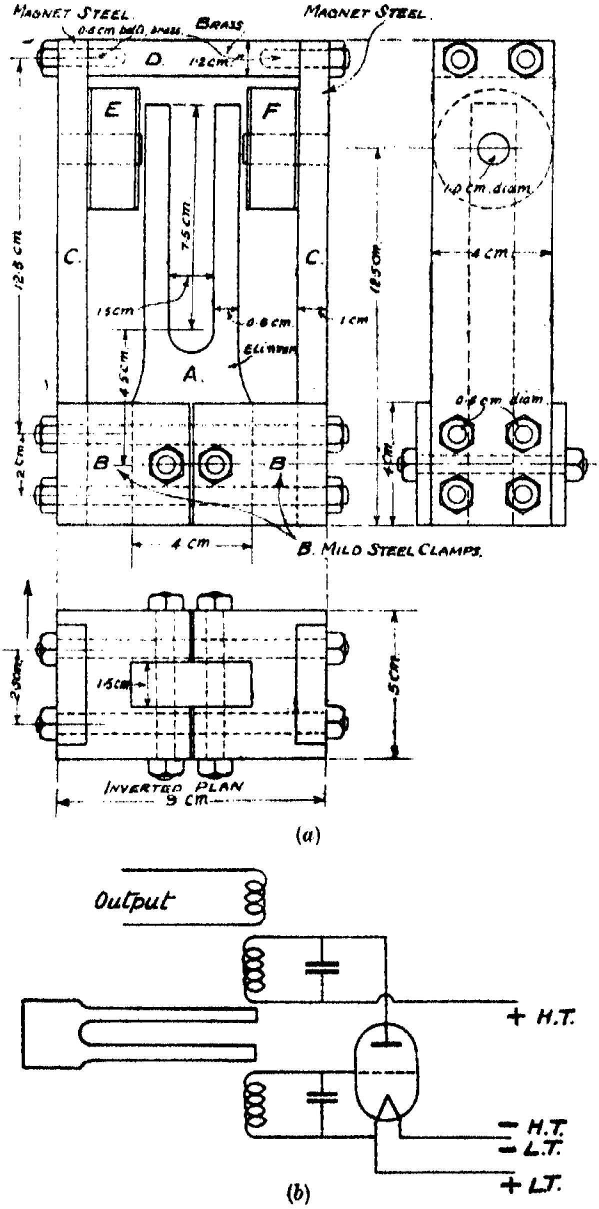
The tuning fork unit is clamped between felt pads in a brass support, which is fixed to an ebonite panel carrying the valve, terminals, and switches.

The electrical circuit used for maintaining the fork in vibration is shown in fig. 1*b*.

Factors Affecting the Frequency of the Fork.

Two tuning fork units of the type described above were set up in a room of very steady temperature and their output circuits were coupled to a vibration galvanometer. This afforded a simple and accurate means of determining the difference between the frequencies of the forks. One of the forks was maintained under steady conditions of operation while various alterations were made in the mounting and circuit conditions of the other fork, the frequency changes resulting from the alterations being measured. A complete set of observations usually occupied such a short time that any frequency changes due to temperature fluctuations were quite negligible. The temperature coefficients of both the forks were known, however, so that a correction could be applied if necessary. The various factors investigated will be considered separately.

(*a*) *Clamping Conditions—the Balancing of Tuning Forks.*—Previous experience had revealed that the frequency of tuning forks could be changed by several parts in a hundred thousand by clamping the fork unit in its support. This effect was attributed to the vibration of the base of the fork. If the two prongs produce equal stresses in the base, there will be a resultant stress in the direction of the length. This may be assumed to be the balanced condition of the fork. If the stresses are not equal, however, there will in addition be a resultant transverse stress. It was therefore anticipated that the vibration in the base of the fork and hence the frequency change on clamping the fork unit in its supports would be functions of the condition of balance of the prongs. Experiments were made to test whether there was any alteration in the frequency change, when the fork was artificially thrown out of balance by having small pieces of soft wax fixed to one or other of the prongs. This loading of the prongs produced a measurable effect, but uncertainties in the clamping prevented quantitative measurements from being taken. A special system of clamping which magnified the frequency changes was therefore adopted. Two heavy lead blocks about 5 cm. by 5 cm. in section and 27 cm. long were



(*a*)

(*b*)

FIG. 1.—Tuning fork and mounting. (*a*) above and (*b*) below.

clamped by means of bolts passing through the blocks, one on each side of the base of the tuning fork unit. The beat frequency between the fork under test and the standard fork was observed, first with the clamp free and then clamped to the base of the fork unit. The process was repeated with various loads of wax attached first to one prong and then to the other prong of the fork. The change of frequency in the unclamped condition due to the addition of the load was used as a measure of the added mass, which needed neither to be known nor evaluated. Although the frequency change was in the same direction for a load on either prong, for purposes of plotting the results it was taken as negative for one prong and positive for the other. When the frequency change due to clamping was plotted as ordinate and the frequency change due to loading as abscissa, a smooth curve very nearly parabolic was obtained. In fig. 2 the dotted line is such a curve obtained for the fork in its original condition. It is seen that when the fork was not loaded, a frequency change of 0·1 cycles was produced by clamping, but that when a load sufficient to change the frequency by 2·5 cycles per second was placed on the grid prong, the change of frequency produced by clamping was reduced to 0·003 cycles. This change in balance was effected without changing the frequency of the fork by filing the base of the grid prong and the top of the anode prong by

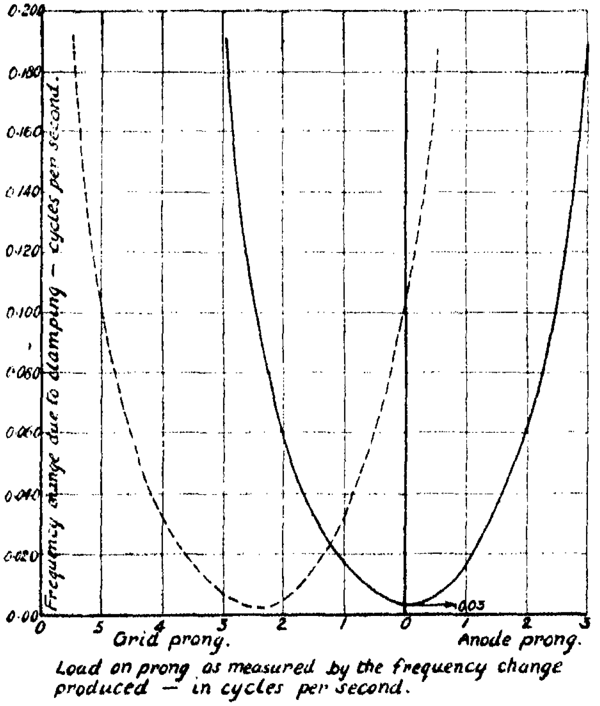


FIG. 2.—Tuning fork balance curves.

amounts producing frequency changes of 1·25 cycles per second. The continuous curve was taken after the fork had been balanced.

A number of tuning forks of similar construction were tested and found to give similar balance curves. In one or two instances difficulty was experienced in obtaining a smooth curve. This was found to be due to a faulty fit of the fork in the base of the unit. The unit was strained by the clamping of the weights and small irregular changes of frequency occurred, masking the true balancing effect. The best results were obtained when the base of the unit was made so that it gripped the fork over two small plane areas about one-third of the way up the base of the fork. The two bottom bolts only, fig. 1*a*. were then used for clamping the fork in its unit.

It was noticed during these experiments that the fork vibrated more readily after its prongs had been balanced, owing probably to a reduction in its logarithmic decrement. To test this, the decrement of a tuning fork was measured by the method described in a later section of the paper, when its prongs were loaded and unloaded. The following results were obtained :—

	Logarithmic decrement.
Prongs unloaded	$6 \cdot 25 \times 10^{-4}$
Grid prong loaded	$7 \cdot 8 \times 10^{-4}$
Anode prong loaded	$7 \cdot 1 \times 10^{-4}$

It was found later that in order to balance the prongs of this fork a load equal to about one-third of the load used in the decrement experiments was required on the anode prong. It appears probable that the fork prongs could be balanced by measuring the logarithmic decrement for various loads on the prongs, but this method is so laborious compared with the one previously described that a complete set of observations was not made.

A considerable number of tuning forks have now been balanced at the Laboratory, and in nearly every one the frequency change produced by clamping the heavy lead blocks to the base of the fork unit was reduced to a few parts in 10^6. When the fork is in this condition the frequency is nearly independent of the manner in which the unit is supported, and any changes occurring during the life of the fork in the bolting of the fork in its unit, or in the clamping of the complete unit in its support, can cause only very small changes of frequency.

(*b*) *Polarizing Magnetic Field.*—In the previous paper (Dye, *loc. cit.*) a curve is given showing the variation of the frequency of a tuning fork as the field strength between the prongs of the fork and the iron cores was varied from

2700 to 1500 gauss. As a new type of fork and much smaller field strengths were now being employed, it was thought advisable to repeat the measurements under the new conditions. The frequency variations were measured as the field strength was varied from 1350 to 400 gauss. The results were plotted and found to form an exact continuation of the previous curve. The rate of frequency variation decreased with decreasing field strength, and for the smallest field strengths used a 10% change produced a frequency change of only 5 parts in 10^6. If the magnets are suitably treated before use, and are not subsequently subjected to the influence of demagnetizing fields or rough treatment, they should remain constant to 1% for periods of more than a year. The frequency instability due to weakening of the magnets should therefore be less than 5 parts in 10^7 over yearly periods.

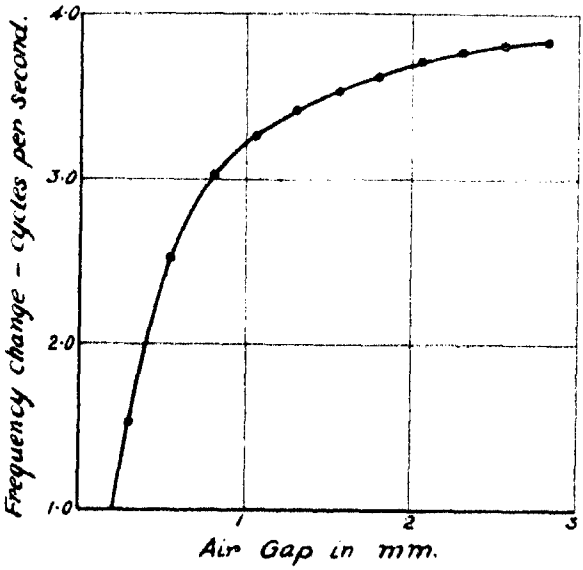


FIG. 3.—Variation of frequency with air gap.

(c) *Air Gap.*—Measurements of the frequency change with air gap were not made with the type of fork described in this paper, owing to the difficulty in making the air gap adjustments. The results of measurements made with a different type of fork provided with adjustable air gaps are included here however, fig. 3, as they show in a marked manner how the rate of the variation of frequency decreases with increasing air gap. To minimize the effect of changes in air gap with time, it is necessary to employ the largest value giving a suitable amplitude of vibration of the fork. That part of the frequency change due to the change in the polarizing field strength resulting from the alteration in air gap was not determined.

(*d*) *Amplitude.*—When the tuning fork is maintained in oscillation by a valve it is impossible to vary the amplitude of vibration of the fork without making mechanical or electrical adjustments in the fork unit or its associated electrical circuit. As these adjustments may themselves affect the frequency of the fork, it is difficult to determine the frequency changes due solely to the changes in amplitude. The fork was, therefore, used as a resonator in the manner shown in fig. 4*a*, and described in detail in the section dealing with logarithmic decrement. The change in amplitude was then effected by altering only the current in the inducing coil A. The amplitude was measured at the top of the fork prongs by means of a microscope. The frequency was found to increase linearly with decreasing amplitude, the change being 14 parts in 10^6 for a change in amplitude from 0·048 to 0·028 mm.

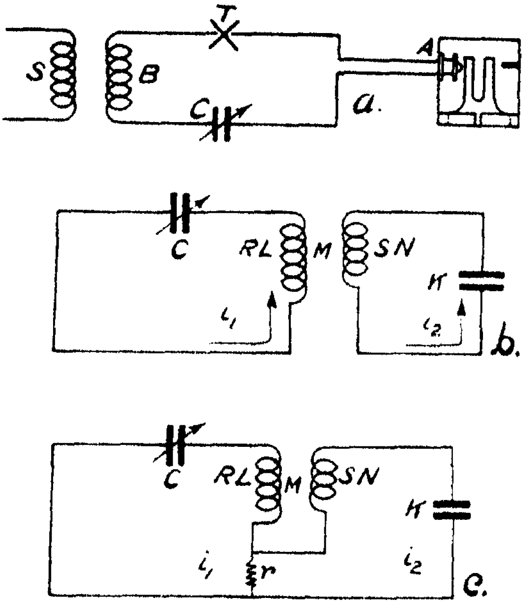


Fig. 4.

(*e*) *Atmospheric Pressure.*—It was anticipated that the frequency of the fork would vary with the atmospheric pressure owing to the loading effect of the atmosphere on the fork prongs. One of the forks was therefore mounted in an enclosure which could be evacuated, and its pressure coefficient was measured between atmospheric pressure and a pressure of less than 1 mm. of mercury. It was found to be strictly linear and was $-2\cdot4$ parts in 10^6 per 1 cm. of mercury increase in pressure. The coefficients of several forks of the same design were measured, and were found to lie between −2 and −3 parts in 10^6; but it is possible that the values of the coefficients of forks of different dimensions might differ appreciably. It is evident that if a tuning fork is to be used as a primary frequency standard it must be installed in a constant pressure enclosure.

(*f*) *Valve Constants—Voltage.*—It was pointed out in the previous paper (Dye, *loc. cit.*) that variations of frequency with anode and filament voltages are a function of the capacitances in parallel with the anode and grid windings of the tuning fork. It can be shown from theoretical reasoning that by adjustment of these capacitances a condition can be obtained in which the frequency is independent of the grid and anode conductances. One would expect this to be the condition of independence of frequency with respect to filament and anode voltages. The expressions obtained were involved and the precise conditions were not worked out. The problem was attacked experimentally by obtaining two sets of curves, one showing the variation of frequency with anode voltage for various values of the grid and anode capacitances, and the other showing the variation of frequency with the filament voltage under the same conditions. From an inspection of the curves it was possible to choose values of the capacitances such that a 10% change of anode voltage produced a frequency change of a few parts in 10^7, and a 10% change of the filament voltage produced a change of 1 part in 10^6. With the coils used no condition of perfect independence of voltage could be obtained. It is possible that this is a result of the variation of frequency with amplitude of the fork; or it may be that the fork failed to drive with the conditions necessary to produce compensation as a very weak driving force was purposely employed. The investigation was not pursued any further as it was thought that instability from other causes would exceed that due to voltage variations. It was found later, however, that small voltage variations formed the chief cause of short period instability in the fork frequency, and the matter might usefully be further investigated.

(*g*) *Loading of the Output.*—The primary frequency standard was intended to provide at any time several supplies of the 1000 cycles per second alternating current for various uses in different parts of the Laboratory. It was therefore necessary to make the frequency of the standard independent of the load applied to it.

Different loads placed on the output winding of the fork were found to produce frequency changes of the order of 1 part in 10^5. A small load such as the grid filament resistance of a valve produced a change of 1 or 2 parts in 10^6. When the output of the fork was connected across the grid and filament of a valve, then loading the secondary of a transformer in the anode circuit of this valve produced frequency changes of only a few parts in 10^7. Connecting a valve to the secondary of the transformer produced a change of 1 part in 10^7. It was thus evidently necessary to interpose a "buffer" valve between the fork and the output circuits to realize a frequency stability of 1 part in 10^7.

The Logarithmic Decrement of Tuning Forks.

A very important factor governing the performance of an oscillator as a frequency standard is its logarithmic decrement. The lower the decrement the less will be the power needed to maintain it in oscillation, and the less dependent will be its frequency on the circuit conditions. It was thought desirable, therefore, to measure the decrement of the fork unit, and determine how it might be reduced. The decrement of the fork unit is greater than that of the fork proper, owing to the pull of the magnets on the prongs of the fork. The method of measurement is analogous to that used for determining the logarithmic decrement of quartz resonators.* There is the difference that the tuning fork is coupled to an external tuned circuit magnetically, while the quartz resonator is coupled capacitively.

The grid and anode coils of the tuning fork unit were removed and a coil of 800 turns was wound on one of the formers. (Coil A in fig. 4*a*.) This coil was connected in series with a condenser C, an inductance coil B, and a thermo-junction T. A constant e.m.f. was induced into B from an external oscillator by means of the coil S. The circuits were arranged so that there was no direct coupling between S and the tuning fork. The frequency of the oscillator was varied slowly in the region of the fork frequency, the circuit being maintained in resonance by adjustment of the condenser C. When the frequency of the oscillator approached the natural frequency of the fork, there was a decrease in the current flowing round the circuit, and a crevasse was obtained in the resonance curve obtained by plotting the frequency of the oscillator against the galvanometer reading. The resonant circuit was tuned to a frequency corresponding to the bottom of the crevasse. The condenser C was then left unaltered while the frequency of the oscillator was varied and the crevasse curve plotted. A square law scale was used with the galvanometer and the scale readings were therefore proportional to the root mean square of the current flowing in the circuit. In practice it was found convenient to plot the frequency against a quantity σ where σ is the ratio of the root mean squares of the currents flowing in the circuit when the fork is free to vibrate and when its prongs are rigidly fixed. A typical crevasse curve is reproduced in fig. 5. It is seen that the whole width of the crevasse is contained in a frequency band of 1 cycle per second.

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* Dye, 'Proc. Phys. Soc.,' vol. 38, p. 399 (1926).

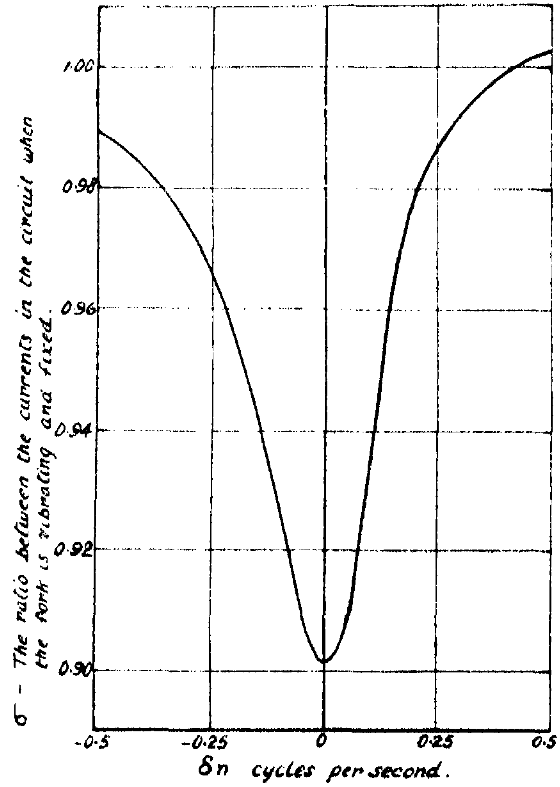

FIG. 5.—Crevasse curve of a tuning fork.

When the prongs of the fork were fixed, the galvanometer reading was practically constant over the frequency band occupied by the crevasse. The coupling was adjusted to make this reading correspond to 100 divisions on the galvanometer scale. The values of σ were then read directly as the galvanometer deflection × 0·01.

If we represent the tuning fork unit by a series combination of resistance inductance and capacitance, S, N, and K, the circuit diagram will be as shown in fig. 4*b*. R, L, and C and S, N, and K are the total resistances, inductances, and capacitances in the circuits. L is the inductance of the two coils A and B in fig. 4*a*. Let e be the instantaneous induced e.m.f. Then the equations of the circuits are

$$i_1\left(\mathrm{L}\alpha + \mathrm{R} + \frac{1}{\alpha \mathrm{C}}\right) - i_2 \mathrm{M}\alpha = e \tag{1}$$

$$i_2\left(\mathrm{N}\alpha + \mathrm{S} + \frac{1}{\alpha \mathrm{K}}\right) - i_1 \mathrm{M}\alpha = 0, \tag{2}$$

where $\alpha = j\omega$.

When the prongs of the fork are clamped the circuit SNK may be regarded as open and the equation of current becomes simply

$$i_0\left(\mathrm{L}\alpha + \mathrm{R} + \frac{1}{\alpha \mathrm{C}}\right) = e. \tag{1A}$$

Eliminating i_2 from (1) and (2) and using (1A) to obtain the value of I_0^2 we have

$$\sigma^2 = \frac{\mathrm{I}_1^2}{\mathrm{I}_0^2} = \frac{(q^2+\phi_2^2)(\phi_1^2+p^2)}{(pq - \phi_1\phi_2 - \mathrm{KCM}^2\omega^4)^2 + (\phi_1 q + \phi_2 p)^2}, \tag{3}$$

where I_1 and I_0 are the root mean squares of the currents when the prongs are free to vibrate and when they are fixed, and the following abbreviations have been introduced :—

$$1 - \mathrm{LC}\omega^2 = p$$
$$1 - \mathrm{NK}\omega^2 = q$$
$$\mathrm{RC}\omega = \phi_1$$
$$\mathrm{SK}\omega = \phi_2.$$

$\pi\phi_2$ represents the logarithmic decrement of the fork and $\pi\phi_1$ the logarithmic decrement of the tuned circuit. The latter quantity was easily determined in a separate experiment. p and q are small quantities and under the conditions of the experiment are equal, since the original tuning makes $\mathrm{LC}\omega^2 = \mathrm{NK}\omega^2$. Since also $p^2 \ll \phi_1^2$ the equation becomes

$$\sigma^2 = \frac{q^2+\phi_2^2}{\left(\phi_2 + \dfrac{\mathrm{KCM}^2\omega^4}{\phi_1} - \dfrac{q^2}{\phi_1}\right)^2 + \left[q\left(1+\dfrac{\phi_2}{\phi_1}\right)\right]^2}. \tag{4}$$

If we substitute $\sigma = \sigma_m$ when $q = 0$ we obtain the expression for ϕ_2

$$\phi_2 = q\sigma_m \sqrt{\frac{1-\sigma^2}{\sigma^2 - \sigma_m^2}}.$$

Now as q is small it is approximately equal to $2dn/n$ where n is the frequency corresponding to the minimum of the crevasse curve and dn is the difference of frequency from that value. The width of the crevasse Δn is equal to $2dn$ and we have therefore

$$\phi_2 = \frac{\Delta n}{n} \sigma_m \sqrt{\frac{1 - \sigma^2}{\sigma^2 - \sigma_m{}^2}}. \tag{6}$$

ϕ_2 was evaluated from the observed values of Δn and σ, and was found to be constant for measurements made at different points on the crevasse curve.

It will be noticed that equation (4) represents a symmetrical curve the value of σ being independent of the sign of q, while the curve actually obtained is slightly asymmetrical. It was thought that this asymmetry might be due to losses in the magnetic part of the circuit, and to account for these losses theoretically, the equivalent electrical circuit of the fork was modified as in fig. 4*c*. The expression for σ^2 then becomes

$$\sigma^2 = \frac{q^2 + \phi_2{}^2}{\left[\phi_2 + \frac{\mathrm{CK}\omega^2}{\phi_1}(\mathrm{M}^2\omega^2 - r^2) - \frac{q^2}{\phi_1}\right]^2 + \left[q\left(1 + \frac{\phi_2}{\phi_1}\right) + \frac{2r\mathrm{MCK}\omega^3}{\phi_1}\right]^2}. \tag{7}$$

writing

$$\mathrm{M}^2 = k^2\mathrm{LN},$$

and

$$\frac{r}{\mathrm{M}\omega} = \phi_3,$$

this becomes

$$\sigma^2 = \frac{q^2 + \phi_2{}^2}{\left[\phi_2 - \frac{q^2}{\phi_1} + \frac{k^2(1 - \phi_3{}^2)}{\phi_1}\right]^2 + \left[q\left(1 + \frac{\phi_2}{\phi_1}\right) + \frac{2\phi_3 k^2}{\phi_1}\right]^2}. \tag{8}$$

The three unknown constants, ϕ_2, ϕ_3, and k in this equation were determined from three points on the experimental curve. The curve then obtained from the equation fitted the experimental curve very closely. The value of ϕ_2 determined from equation (8) agreed within the limits of accuracy of the experiments with the values obtained from the approximate expression (6) which was therefore used for future measurements.

A number of measurements made under the same conditions gave results agreeing to $\pm 1\%$, which indicates the accuracy of the decrement determinations.

The logarithmic decrement was determined for different values of the polarizing field strength. The results are given in Table I.

It is seen that a considerable decrease in the decrement of the fork unit is effected by the reduction of the field strength.

The effect of the amplitude of vibration of the fork on the decrement was then investigated. The change in amplitude was effected by altering the coupling

Table I.—Variation of the Logarithmic Decrement of the Tuning Fork with the Intensity of the Magnetic Field.

Magnetic field in gauss	230	350	610	770	810
Log. dec. × 10^4	3·96	4·44	6·80	8·17	9·05

between the external oscillator and coil B. The whole of the crevasse curve was thus obtained on a smaller scale for the smaller amplitudes. The oscillator frequency was adjusted to obtain the bottom of the crevasse, and the amplitude at the ends of the prongs of the fork was then measured by means of a microscope. The results given in Table II indicate that between the limits investigated there is a small change of decrement with the amplitude.

Table II.—Variation of Logarithmic Decrement with Amplitude.

Amplitude in mm.	0·025	0·031	0·043
Log. dec. × 10^4	7·42	7·65	7·75

Final Design of Tuning Fork Equipment.

In the light of the foregoing experiments a number of alterations were made to the tuning fork unit and its electrical circuits. The magnets were left unaltered as they had probably reached a thoroughly stable condition after their ten years' service. The polarizing field strength was, however, decreased to the order of 400 gauss by increasing the air gaps to 5 mm. The base of the fork unit was cut away so that the fork was gripped only at two small areas of its base. Only one pair of bolts was used as shown in fig. 6. This method of gripping the fork is not necessarily the best, but it was found that good balance curves could be obtained by its use and it was effected without any serious modification in the existing design. The essential features are a good fit between the surfaces in contact and the removal of these clamping surfaces to a greater distance from the base of the prongs. The most suitable capacitances for the grid and anode circuits were chosen. The values were found to be 0·01 μF. across the anode winding and 0·0022 μF. across the grid winding. The fork prongs were then carefully balanced, the fork frequency being adjusted during the process to have its nominal value of 1000 cycles per second at a temperature of 21° C. and a pressure of 720 mm. of mercury. The unit was then installed in a temperature regulated air-tight enclosure, the general arrangement being shown diagrammatically in fig. 7. It was fixed in a horizontal position in brass supports being separated from the metal of the supports by thick felt pads which served to damp down any

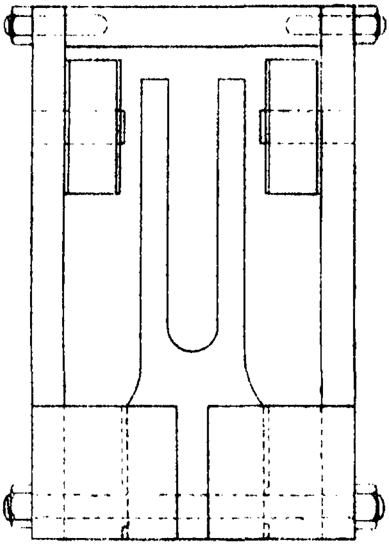

Fig. 6.—Tuning fork unit.

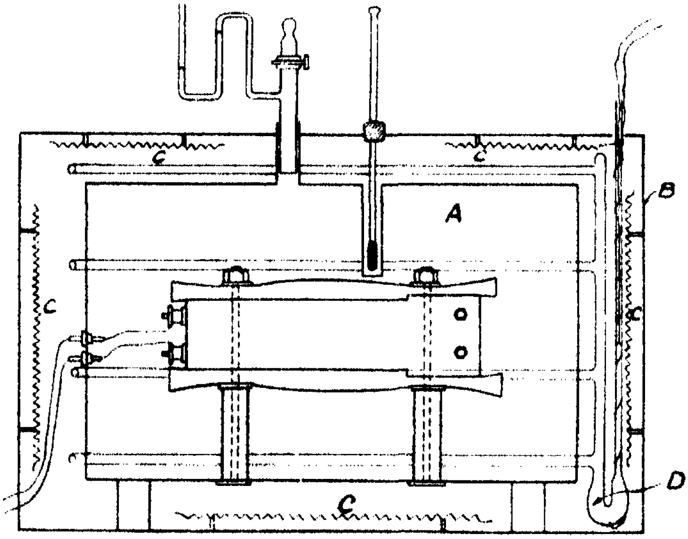

Fig. 7.

residual vibration of the unit and also to protect the fork from external vibration. Silk tape was bound round the unit to prevent any dust or felt fibres from reaching the prongs of the fork. The anode and grid condensers were attached to the brass supports, which were fixed rigidly in a stout copper air-tight box A. This was surrounded by another copper box B, the heating mats C and a thermal regulator D being disposed in the space between the two. There were heating mats on all six walls of the box. The thermal regulator was of the toluene mercury type and was built from glass tubing in the form of a rectangular box around the inner copper container. A thermometer reading to 0·02° C. was inserted in a tube sealed into the inner box, the bulb of the thermometer being near the tuning fork. The whole equipment was contained in a wooden enclosure. The pressure inside the inner box was reduced to about 720 mm. of mercury, the pressure being indicated by a manometer.

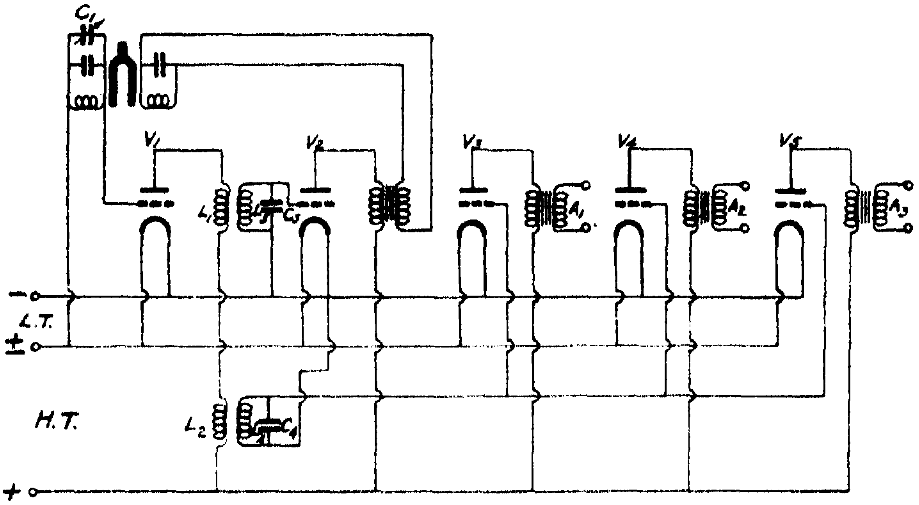

FIG. 8.—Tuning fork and amplifier circuits.

The electrical circuit adopted for driving and taking power from the fork is shown in fig. 8. The output coil of the fork is not used, but power is taken from a coil L_2 in the anode circuit of valve V_1. The coils L_1 and L_3, both of 30 mh. inductance, are disposed so as to have no coupling between them. The circuits L_3 C_3 and L_4 C_4 are tuned to 1000 cycles per second. By varying the coupling between L_1 and L_3 the amplitude of the fork vibrations can be regulated and by varying that between L_2 and L_4 the amplitude of the output can be varied. The frequency of the fork varies with the coupling, so that the position of the coils must be fixed when the best conditions have been chosen. Three outputs A_1, A_2, A_3 are taken through buffer valves V_3, V_4, V_5. A portion of the capacity across the grid winding of the fork consists of a variable condenser C_1 of about 500 μμF., which is mounted on the panel outside the constant temperature enclosure. This forms a very convenient means of making small adjustments to the fork frequency, the total adjustment possible being 30 parts in 10^6.

Two of the three outputs are connected to the multivibrator and phonic motor while the third is connected to a small amplifier which supplies the 1000 cycle note for any other purpose for which it may be required. These output leads are permanently connected, and switching on the various subsequent valves produces a frequency change of only a few parts in 10^8. Other vibrators of 1000 cycles per second are frequently in use at the Laboratory, and in order that these should not react on the frequency of the standard fork owing to coupling between the various output leads, these leads are all carefully screened.

The voltage supplies for the tuning fork and a phonic motor amplifier are obtained from batteries which are maintained in a permanently charged condition by means of a supply obtained from the A.C. mains.

The Chronograph for measuring the Frequency of the Fork.

For the purpose of determining the frequency of the tuning fork, a special chronograph was designed. One of the outputs from the fork is used after amplification for driving a phonic motor. The motor has 100 teeth and makes 10 revolutions per second, or more exactly per 1000 vibrations of the fork. A spindle is geared down by a worm and wheel to make one revolution per second. This spindle carries a drum which revolves with the spindle by means of a magnetic drive. A clutch is provided for weakening the drive and the drum can then be stopped for inspection without stopping the phonic motor. The marking pen is mounted on a carriage which is moved along in a direction parallel to the axis of the drum at the rate of 1 mm. per hour. The drum is 18 cm. long so that each record lasts a week. The hour spindle used for moving the marker also serves to close a contact for a few seconds once during each hour. Seconds impulses from the Shortt clock then operate the pen, recording a mark on the paper carried on the drum of the chronograph. The four or five impulses usually obtained, owing to the duration of the hourly contact, merely serve to accentuate the mark. The diameter of the drum is 5 cm. so that the paper travels a distance of 600 m. per hour. If the rates of the Shortt clock and the tuning fork are the same, the marks form a line parallel to the axis of the drum. A difference in rate of 0·086 second per day produces a slope of about 30°. This corresponds to a fork frequency differing by 1 part in 10^6 from the nominal value of 1000 cycles per second, if the Shortt clock rate is assumed to be zero. If the slope of the line is not too great, it is possible to read off the frequency of the fork by inspection of the record with an accuracy of 1 part in 10^7. It is usually necessary to apply a small correction for the rate of the Shortt clock. The chronograph may be used to compare the rate of the tuning fork with that of any time or frequency standard which furnishes accurate second impulses. Additional contacts on the hour spindle enable more than two standards to be compared at the same time.

A chronograph record showing the relative rate of the fork and Shortt clock is reproduced in fig. 9. The upper row of vertical strokes records the impulses received hourly from the pendulum of the Shortt clock. Small irregularities are known to occur in the signals received from the Shortt clock which are obtained from the slave pendulum, and these account for some of the irregularities in the record.

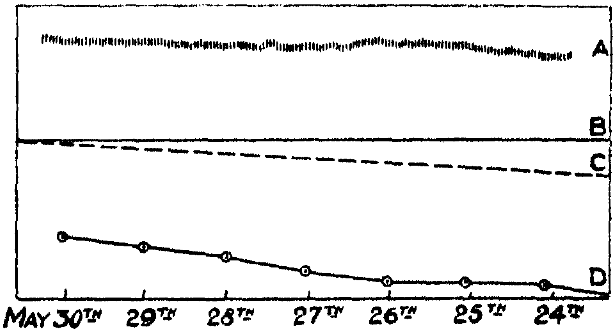

FIG. 9.—Record ending 9 a.m., May 30, 1932. A—Signals recorded hourly by Shortt clock seconds; the slope gives the rate between the clock and the fork. B—Reference line of zero rate. C—Slope to represent a rate of 1 part in 10^7 or 0·009 seconds daily. *D—The rate of the Shortt clock as measured by the daily time signals.*

Performance of the Tuning Fork.

Long Period Stability.—The tuning fork has now been in continuous operation for nearly two years, and a considerable amount of data concerning its frequency stability has been collected. The frequency of the fork is determined each day from the chronograph records, and daily readings are also taken of the anode current taken by the five valves on the fork panel and of the pressure and temperature inside the enclosure. The largest changes of frequency that have occurred were due to the renewing of the valves which was necessary after every three or four months. During the life of the valves the anode current very gradually decreased, causing a gradual change in frequency. It was found, however, that when the anode current was maintained at a steady value by adjusting a rheostat in series with the valve filaments, the frequency change due to this effect was almost entirely eliminated. A rapid decrease in the anode current indicated that the valves were nearing the end of their lives, and they were then replaced. The first valves used were replaced by a later and very different type. To obtain the same amplitude of vibration of the fork, the coupling between the coils L_1 and L_2 was decreased and the anode voltage was decreased from 50 to 40 volts. As a result of these changes the fork frequency increased by nearly 1 part in 10^5. When the new valves had been in operation for about 100 hours, the frequency of the fork was brought back to its nominal value by adjustment of the grid condenser. On subsequent occasions the valves were replaced by new ones of the same type with resulting frequency changes of 1 or 2 parts in 10^6 which were again compensated for by adjustment of the grid condenser. Apart from these changes there has been no general drift in the fork frequency amounting to more than 1 part in 10^6, and for periods of as long as six weeks the frequency has been constant to 2 or 3 parts in 10^7. During the period from December 28, 1932, to February 4, 1933, the rates of the tuning fork and the Shortt clock were very nearly the same, and the total variation between time as represented by the fork and as given by the clock signals amounted to only 0·05 second. Variations of frequency of 1 or 2 parts in 10^7 usually occur, however, in the course of a week owing to changes in temperature, pressure, or voltage supplies. The frequency changes due to temperature are usually negligible. The temperature coefficient of the tuning fork is +16 parts in 10^6 per 1° C. rise in temperature, so that for a frequency stability of 1 part in 10^7, the temperature must remain constant to 0·006° C. When the mercury in the regulator is clean no change in the thermometer reading can be observed during periods of several months, and any frequency instability due to temperature is probably less than 1 part in 10^7. Trouble in the temperature regulation has occurred on several occasions, however, and it has been necessary to clean the mercury in the regulator.

The fork enclosure was not originally designed for maintaining a constant pressure and is built of too flexible a material for this purpose. The result is that although the enclosure is air-tight the pressure inside varies by about one-tenth of the variations of atmospheric pressure. The pressure in the enclosure thus varies by two or three millimetres, causing frequency changes which may amount to as much as 6 parts in 10^7.

The voltage of the mains supply varies with the load, and the small currents maintaining the batteries in a charged condition are not constant. As a result, variations of 2% may be produced in the voltage of the batteries causing corresponding frequency variations of several parts in 10^7. In Table III a typical set of observations made during a week is reproduced.

Short Period Stability.—Measurements at radio frequencies for which high harmonics of the tuning fork are used as the standard frequencies, are usually completed in a few seconds. It is essential, therefore, to have information concerning not only the daily rate of the fork, but also the frequency stability over short periods.

The short period frequency stability of the tuning fork was examined by comparison with a quartz crystal oscillator. The frequency of this oscillator was 20,000 cycles per second. In order to obtain seconds impulses from the oscillator, it controlled another oscillator at a frequency of 1000 cycles per second which drove a phonic motor. To enable accurate measurements to be made at about 1 minute intervals, beats were counted between the twentieth harmonic of the fork and the quartz oscillator. A frequency difference of 1 part in 10^6 then gave a beat lasting 50 seconds. The duration of the beat was measured with an accuracy of 0·1 second giving an accuracy of frequency comparison of 2 parts in 10^9.

Table III.—Rate of Tuning Fork during the week ending October 17, 1932.

Date.	Temperature °C.	Pressure mm. of Hg.	Anode current in m.A.	Rate of fork relative to Shortt clock parts in 10^7.	Rate of clock relative to time signals parts in 10^7.	Rate of fork relative to time signals parts in 10^7.
11.10.32	20·38	722	3·19	+2	−1	+1
12.10.32	20·38	720	3·18	+5	−5	0
13.10.32	20·38	720	3·17	+5	−5	0
14.10.32	20·38	720	3·16	+2	−2	0
15.10.32	20·38	721	3·16	+2	−3	−1
16.10.32	—	—	—	+3	−2	+1
17.10.32	20·38	721	3·16	+2	−4	−2

In columns 6 and 7 the corrected time signals have been used.

The results of one set of observations are shown in fig. 10. It is seen that though the mean frequency difference during the first 25 minutes differed by only 1 part in 10^8 from that during the second 25 minutes, yet there are irregular variations of frequency difference of ± 2 parts in 10^8. The measurements were repeated and during the observations the filament voltage applied to the tuning fork was measured against a standard cell. The voltage was found to fluctuate in precisely the same manner as the frequency, and by the amount required to produce the observed frequency changes. Another set of observations was then taken, the filament voltage being maintained at a constant value by hand manipulation of a fine rheostat. It was possible to secure a voltage constancy of 0·0002 volt, which was calculated to reduce the frequency fluctuations to the order of 1 part in 10^9. A smooth curve could then be drawn through the observed points such that no point was removed from it by more than 1 part in 10^9. A periodic change in frequency which it had been impossible to detect previously was then revealed. The amplitude of this frequency change was 1 part in 10^8 and the period was 20 times as great as the mean period of beat at 20,000 cycles per second. It was evident, therefore, that there was a very small reaction between the tuning fork and the 1000 cycles per second oscillator controlled by the quartz crystal. To show the effect more clearly the coupling between the two oscillators was purposely increased by removing the earth connection from the screens of the various output leads from the fork. The results shown in fig. 11 were then obtained. The amplitude of the frequency cycle was increased to 5·6 parts in 10^7 although the mean difference between the frequencies of the two oscillators was only 4·5 parts in 10^7. The period of the frequency cycle agreed exactly with the period of 1 beat at 1000 cycles per second. If the frequency difference was changed to about 5 parts in 10^6, and the coupling was still further increased, then the amplitude of the cyclic variation could be increased to 5 parts in 10^6 before the two oscillators were eventually pulled into step.

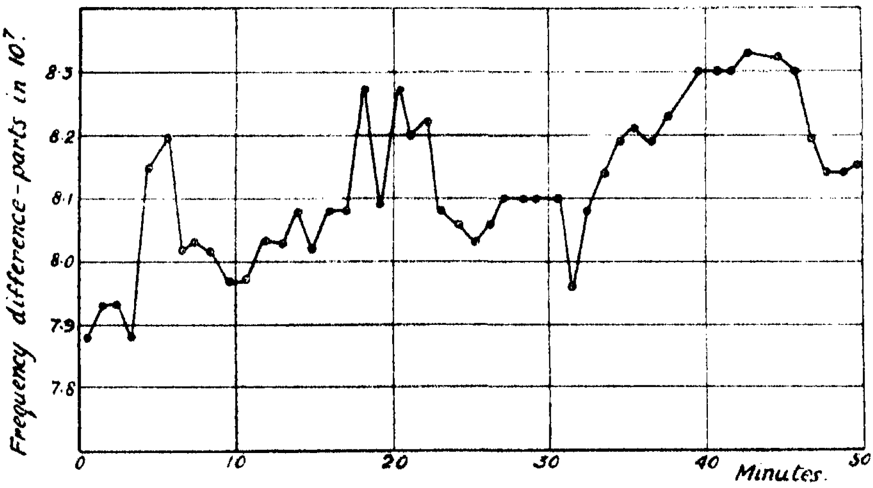

FIG. 10.

Conclusion.

The performance of the tuning fork has been so much better than was expected that two sources of frequency variation, which at one time were thought to be negligible, have proved to be the main cause of instability of the fork frequency. These two sources of variation, small changes in the supply voltages and in the pressure, could both be almost entirely eliminated; but as the fork has been in continuous use as a frequency standard it has not been convenient to carry out the necessary improvements. The evidence suggests that were the improvements effected, a frequency stability over long periods of 1 part in 10^7 and over short periods of a few parts in 10^9 would be obtained.

The frequency of the fork in comparison with the N.P.L. Shortt clock can be measured at any time with an accuracy of 5 parts in 10^8. It is necessary to apply a correction for the rate of the Shortt clock, and the ultimate accuracy with which the absolute value of frequency is known depends on the accuracy of the time signals which are used to determine the rate of the clock. The final frequency can, however, usually be ascertained with an accuracy of ± 1·5 parts in 10^7. In its present condition the tuning fork maintains a frequency stability of the order of 3 parts in 10^7 over periods of a week or more.

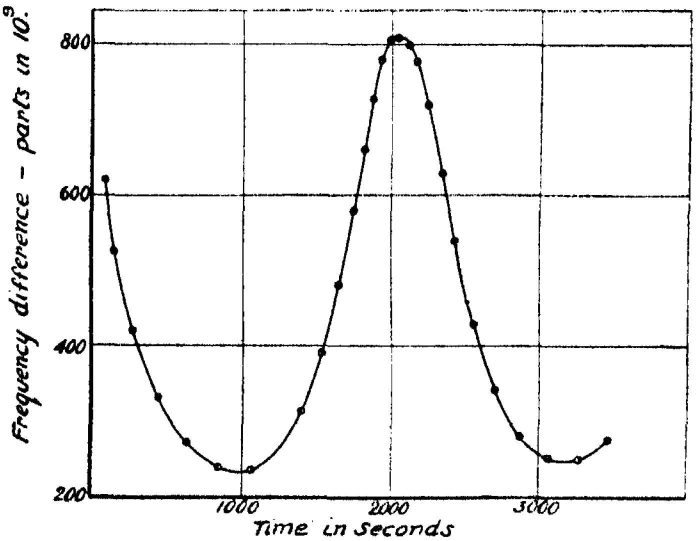

FIG. 11.

The fact that the frequency of the tuning fork is dependent on the valves in the electrical circuit, and that these valves have to be renewed after periods of several months, prevent the fork from being used at present as a long period time standard. The tuning fork itself as a mechanical vibrator is so stable that it has not yet been possible to measure its stability owing to the small frequency changes of the order of 1 or 2 parts in 10^8, which are produced by changes in the electrical circuit.

Acknowledgments.

The work described in this paper was carried out as part of the programme of the Radio Research Board, and acknowledgment is due to the Department of Scientific and Industrial Research for granting permission for publication. The co-author wishes to express his deep indebtedness to the late Dr. Dye who supervised the whole of the work, and to Dr. L. Hartshorn and Dr. R. L. Smith-Rose for assistance in the course of preparation of the paper.

Summary.

The paper describes the work leading to the installation of a 1000 cycles per second valve maintained tuning fork as a frequency standard in continuous operation at a frequency within 1 part in a million of its nominal value. A method of balancing the prongs of the fork was devised. The vibration transmitted to the base of the fork was thereby reduced to a minimum and the frequency of the fork was nearly independent of the manner in which the fork unit was supported. The variations of the frequency of the fork with polarizing field strength, air gap, amplitude of vibration, atmospheric pressure, the voltage supplies and the loading of the output coil, were investigated.

The logarithmic decrement of the fork was determined for various values of polarizing field.

A description is given of the final design of the tuning fork, of the air-tight and thermostatically controlled enclosure in which it is installed, and of the electrical circuit employed for driving and taking power from the fork.

A chronograph is described which enables the rate between the tuning fork and a standard clock to be read by inspection with an accuracy of 1 part in 10^7, and determined by measurement with an accuracy of 5 parts in 10^8. Details are given of the performance of the fork over a period of 20 months since its installation. The frequency stability over hourly periods is of the order of 5 parts in 10^8, and over weekly periods, 3 parts in 10^7.

The Latent Energy Remaining in a Metal after Cold Working.

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(Received August 31, 1933.)

Summary.

Measurements of the latent energy remaining in metal rods after severe twisting are described. Very much more cold work can be done on a metal in torsion than in direct tension. It is found that as the total amount of cold work which has been done on a specimen increases the proportion which is absorbed decreases. Though saturation was not fully reached even with twisted rods, curves representing the experimental results for copper indicate that it would have been reached at a plastic strain very little greater than the strain at fracture. The amount of cold work necessary to saturate copper with latent energy at 15° C. is thus found to be slightly greater than 14 calories per gram.

By using compression instead of torsion, it was found possible to do much more cold work on copper than this, and compression tests revealed the fact that the compressive stress increases with increasing strain till the total applied cold work was equivalent to 15 calories per gram. No further rise in compressive stress occurred with further compression even though the specimen was compressed till its height was only 1/53rd of its original height.

The fact that the absorption of latent energy and the increase in strength with increasing strain both cease when the same amount of cold work has been applied suggests that the strength of pure metals may depend only on the amount of cold work which is latent in them.

When a metal is subjected to plastic distortion (cold working) most of the work done reappears in the form of heat, but a certain proportion remains latent and is no doubt associated with the changes to which cold working give rise in the physical properties of the metal. When the metal is heated all this latent heat must be released before the melting point is reached, and when it is dissolved the latent heat must appear as a heat of solution. It is therefore possible to measure the latent heat of cold working either when energy is put into the metal or when it is released. In the former case, the work done and the heat evolved during plastic deformation are measured. The difference is the latent energy of cold working. This method has been adopted by Farren and Taylor* and by Hort†, who found that within the range of their experiments 5½ to 13½% of the work done remains latent in the metal.

Some attempts have been made to measure the latent energy of cold working when it is released, but the results are not always comparable with those of Farren and Taylor and when they are the two kinds of measurements do not seem to be in agreement. In the experiments of Farren and Taylor the cold work was done by stretching a rod of metal by a direct load. With such a system of loading only a very limited amount of work can be done on the specimen before it breaks. With copper, for instance, the maximum latent energy which they measured was equivalent to a rise in temperature of only 0·83° C. In order to release the latent energy of copper it is probably necessary to raise its temperature to 500° C. or more. The latent energy would appear as the difference between the amounts of heat necessary to raise the temperature of two equal specimens to 500° when one of them had been subjected to cold work and the other had not. To measure it would be equivalent to measuring the difference between the specific heat of two metals when that difference is only 1 part in 600.

It is difficult to attain such accuracy in heat measurements, but by using metals which have been subjected to much more severe cold working than is attainable under a direct load, greater latent heat can be obtained and the accuracy of the measurements of the energy released on heating correspondingly increased.

It is well known that much more cold work can be done on a metal rod by twisting it than by stretching it. The amount of work which can be done in direct extension depends on the nature of the load-extension curve. The condition for fracture by instability owing to the formation of a local " neck " is

$$\frac{l_0}{\mathrm{T}}\frac{d\mathrm{T}}{dl} < 1 \qquad \text{or} \qquad \frac{d \log \mathrm{T}}{d \log (l/l_0)} < 1,$$

where T is the tensile stress, l is the length, and l_0 the initial length of the test specimen. The criterion for fracture can therefore be found by plotting the load-extension curve on a logarithmic scale. Fracture will then occur when the tangent to the curve makes an angle 45 degrees with the axes. When a round bar is twisted it will not fail owing to the formation of a local neck until the shear stress has ceased to increase with increasing strain. (In fact, twisted specimens usually fail for reasons other than this kind of instability.)

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* 'Proc. Roy. Soc.,' A, vol. 107, p. 422 (1925).

† 'Mitt. Forsch. Arb. deuts. Ingenieur,' vol. 41 (1907).

If the tensile stress rises very rapidly for a very small extension and then continues to rise much more slowly as the strain increases to large values, a tensile specimen will break at a very small extension, but a twisted rod may suffer very great distortion before breaking. The results of tensile and torsion tests on two identical nickel rods are shown in fig. 1. The nickel was used in the hardened condition as supplied by Messrs. Henry Wiggin & Co. In the tensile test the rod suffered no measurable plastic distortion till a stress of 76,800 lbs. per sq. in. was reached. It fractured when the stress was 84,800 lbs. per sq. in., and the extension was then $0\cdot012 l_0$.

In the torsion test the first measurable plastic strain occurred when q, the mean shear stress was 46,000 lbs. per sq. in.; q then gradually increased with increasing twist to 68,000 lbs. per sq. in. when fracture occurred. The amount of twist is expressed in fig. 1 by the non-dimensional quantity ND/l, where N is the number of turns, l the length of the specimen, and D its diameter. It will be shown later that this is π times the shear strain in the surface layers of the rod. The maximum value of ND/l attained before fracture was 0·82.

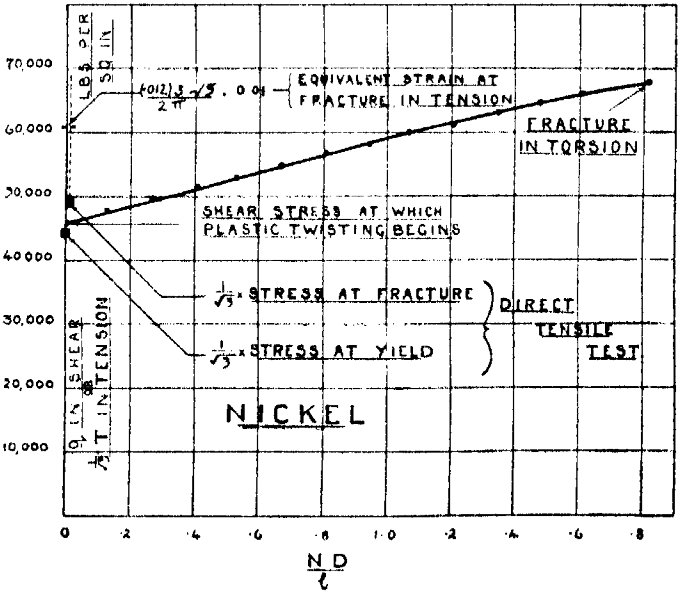

Fig. 1.

In order to represent these two tests on the same diagram the theory of v. Mises may be used. According to this theory if T is the stress at which plastic flow begins in a rod subjected to direct tension and q the shear stress for plastic flow under the action of a pure shear, $q = \mathrm{T}/\sqrt{3}$. Similarly in order to find the small increment in $\mathrm{N}\mathrm{D}/l$ which is equivalent, so far as work done on the specimen is concerned, to a small direct extension $(l - l_0)/l_0$ it is necessary to multiply* by $3\sqrt{3}/2\pi$. The results of the tensile test are represented in fig. 1 by points whose ordinates are $76{,}800/\sqrt{3} = 44{,}300$ lbs. per sq. in. for the plastic yield point and $84{,}800/\sqrt{3} = 49{,}000$ lbs. per sq. in. at fracture. The abscissa representing the strain at fracture is $(0\cdot012)3\sqrt{3}/2\pi = 0\cdot01$.

It will be seen that the total work done on the specimen during the test, which is proportional to the area under the stress-strain curve in each case, is about 80 times as great for the twisted rod as it was for the rod broken in direct tension.

In the work to be described later cold work was done by twisting instead of direct extension. The maximum latent energy left in copper after severe twisting was equivalent to a rise in temperature of about 15° C., *i.e.*, 18 times as much as that used in Farren and Taylor's experiments. The release of this amount of energy can be measured and in a later communication we hope to be able to describe the apparatus with which such measurements have been made.

In the experiments of Farren and Taylor it was found that the energy left in a metal after distortion is a definite fraction of the work done on it. This fraction varied with the nature of the metal, but appeared to be constant for various amounts of distortion in spite of the fact that the resistance to extension rapidly increased as the extension increased. It seems unlikely that it would be possible to increase the amount of latent energy indefinitely by doing cold work; accordingly one of our objectives in measuring the latent energy due to cold work in twisted bars was to find out whether it goes on increasing proportionately to the work done when the cold working is very severe. Work recently published by Rosenhain and Stott† shows that when copper or aluminium wire is drawn through a die a rather smaller proportion of energy is absorbed than was found by Farren and Taylor. In their apparatus the measured work done included the work done against friction between the wire and the die so than the proportion absorbed was necessarily smaller than that measured with apparatus in which all the work is expended in straining the material, but after making due allowance for the friction they still found that the proportion of energy absorbed was rather smaller than that found by Farren and Taylor. The present experiments confirm this result.

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* For $\rho\delta\mathrm{W} = \mathrm{T}\,(l - l_0)/l_0 = \frac{2\pi}{3}\,q\delta\,(\mathrm{N}\mathrm{D}/l)$, see equation (2), p. 315.

† 'Proc. Roy. Soc.,' A, vol. 140, p. 9 (1933).

Measurement of Latent Energy Produced by Cold Work.

To measure the latent energy it is necessary to measure simultaneously the work done and the heat evolved, and in order to avoid loss of heat it is necessary to perform the whole experiment rapidly.

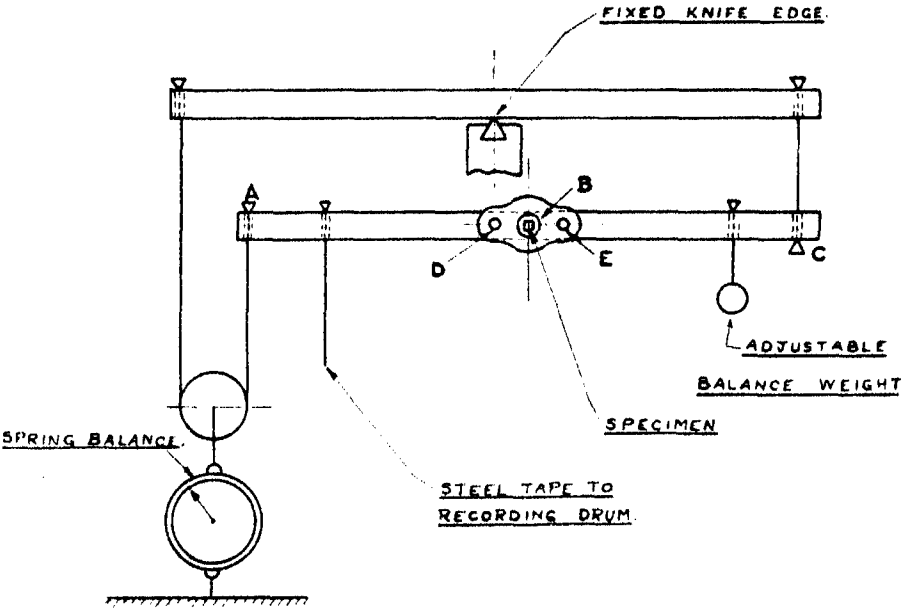

FIG. 2.—Arrangement of torque recorder.

Measurement of Work Done.

To measure the work done during a rapid twisting of a bar, a self-recording machine was designed which produced diagrams in which the ordinates represent torque and the abscissæ angle of twist between two sections of the twisted bar.

The specimens were round in section, ⅜-inch diameter, and had square ends ¾-inch × ¾-inch. Their length was 15 inches, but the round part only occupied 11 inches of this. One square end fitted into the headstock of a lathe and could be twisted at any desired speed by a geared electric motor. The torque was applied at the other end by the lever arrangement and spring balance shown in fig. 2. This was designed to apply a pure couple in such a way that it would be recorded directly as a movement of the spring balance. The diagram is self-explanatory, except for the arrangement of the part where the torque is transmitted to the specimen. The arm, ABC, carries a ball race at B which is housed on the loose headstock of the lathe. It also carries two pins, D, E, which engage with a carrier fitting over the square end of the specimen. This arrangement permits the specimen to extend longitudinally* and ensures that no bending moments are applied. The torque was recorded by means of a steel tape (fig. 2), one end of which was attached to the torque arm, while the other passed round a recording drum which carried the paper on which the record was made.

The twist was recorded by means of two discs which were attached to the specimen at points 10 inches apart. These carried steel tapes, one of which drove a spindle and the other a nut. This nut carried a slide rest to which the recording pencil was attached so that the position of the pencil on the recording drum depended only on the relative rotations of the nut and spindle.

Measurement of Heat Evolved.

Two methods were used. The first was to measure the rise in the temperature of the surface of a specimen after rapidly twisting it through about one turn. The second was to remove it so rapidly from the lathe after finishing the twisting that the heat generated in the central part of the specimen had not penetrated through the square ends, and drop it into a calorimeter. The two methods proved to give results in good agreement with one another.

The first method is the same as that used by Farren and Taylor, but the fact that the specimen is now twisted instead of being pulled introduces a new difficulty. More cold work is done in the outer layers than near the middle of the specimen so that if the experiment is done very rapidly the outer layers are heated more than the inner ones. A certain time must elapse before the temperature is equalized over the cross-section, but the reading must be made before the wave of cooling penetrates from the ends of the specimen to the central part where the temperature measurements are made. The temperature was measured by means of an iron-constantan thermocouple connected directly to a galvanometer.

The movement of a spot of light reflected from the galvanometer mirror was recorded photographically on a drum rotating at a uniform speed.

In the experiments of Farren and Taylor the thermocouple was inside the specimen and its leads passed down the middle of the hollow specimen so that the junction itself and its leads certainly took up the temperature of the specimen. In the case of solid specimens this method of ensuring good thermal contact is not possible. The method adopted in the present experiment was to solder the thermo-junction to the middle of a small square of sheet silver. This was tightly bound by silk threads to the outer surface of the specimen so that the junction itself was on the under side of the silver. The thermocouple wires were insulated from the silver and the specimen by enamel except at the point where they were soldered. This method ensured that the junction was not cooled by conduction along the thermocouple wires.

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* When a bar is twisted plastically it usually grows in length.

In order to remove any further uncertainties that may exist in the use of a thermocouple applied to the outside of a specimen and to allow for cooling of the specimen during the time taken to twist it and for possible cooling of the thermocouple by the silk threads which bound it to the specimen, the heat input corresponding with the observed temperature-time curve was determined independently after each experiment. For this purpose the temperature-time record and the torque-angle curve were taken for, say, one turn of the lathe head. The specimen and its thermocouple were then removed from the torque apparatus and after cooling a heavy current up to 100 amperes was passed through the specimen and maintained for the same length of time as that for which the torque had been applied. By adjusting this heating current it was found possible to reproduce exactly the temperature-time curve obtained in the torque test provided the twisting had not been carried out so quickly that the equalization of temperature between the outside and inside of the specimen could not take place. The current and the potential drop between the square ends of the specimen were then measured and the energy input calculated.

The cooling is due chiefly to conduction from the ends of the specimen. It was shown by one of the present writers that during a time equal to $T = 0{\cdot}014\rho\sigma l^2/\kappa$ after the generation of heat the cooling effect of the ends causes a drop in temperature in the middle of the specimen which is less than $0{\cdot}6\%$ of the total rise. In this expression l is the length of the specimen which in the present case is 30 cm., for iron $\rho = 7{\cdot}8$, κ the conductivity is $0{\cdot}14$ and σ the specific heat is $0{\cdot}106$ so that $T = 80$ seconds.

In the temperature-time record, fig. 3, A represents the time at which the twisting began, B represents the time it was complete. The time occupied by the operation, namely, 45 seconds, is considerably less than the 80 seconds necessary for the cooling effect of the ends to penetrate to the middle, yet it is sufficiently long to ensure that the temperature is uniform across the section.

It will be seen in fig. 3 that no measurable drop in temperature occurred till the time represented by C. The time interval between the beginning of the experiment and the first observable drop in temperature was found to be about 95 seconds. This agrees well with the theoretical value $T = 80$ seconds.

For copper specimens, owing chiefly to their greater conductivity, T was only 11·5 seconds; the twisting being carried out in 6 or 7 seconds, leaving 4 or 5 seconds available for the temperature measurement, before the waves of cooling from the ends produced an appreciable effect in the middle.

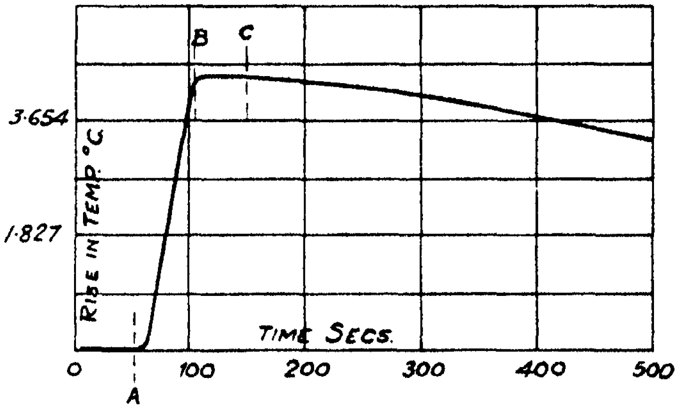

FIG. 3.—Temperature-time record during plastic twisting.

Expression of Results in Non-dimensional Form.

The shear strain at any point in the twisted rod is $2\pi Nr/l$, where N is the number of turns in length l. A non-dimensional expression for representing twist is therefore ND/l. If the shear stress depends only on the shear strain, it may be represented by an expression of the form $q = 12G/\pi D^3$, where D is the diameter of the specimen, G is the applied torque and q is the uniform shear stress which would give rise to the torque G. q is approximately the average shear stress over the cross-section.

Results.—The results of tests on an annealed mild steel bar and on a de-carburized mild steel bar are given in Tables I and II. Each bar was twisted through successive small amounts, usually about 1 turn, and the value of ND/l given in column 1 corresponds with the total strain from the initial annealed condition of the bar. The stress given in column 2 is expressed in lbs. per sq. in. and is the mean value of q between the beginning and end of one experiment, thus referring to Table I the mean value of q during the fifth stage of twisting was 43,700 lbs. per sq. ft. and during this stage the strain increased from $ND/l = 0\cdot1126$ to $ND/l = 0\cdot1452$. The work done during a twist of δN turns is $2\pi G\delta N$ so that the work done on unit mass is

$$\delta W = 8G\delta N/D^2l\rho. \tag{1}$$

Expressed in non-dimensional form

$$\delta W = \frac{2\pi q}{3\rho}\,\delta\left(\frac{ND}{l}\right), \tag{2}$$

where $\delta\,(ND/l)$ is the change in ND/l during the experiment under consideration. If q is expressed in lbs. per sq. in. and δW is expressed in calories per gram of metal

$$\delta W = \frac{2\pi q}{3\rho J}\,\frac{(453\cdot6)\,(981)}{(2\cdot54)^2}\,\delta\left(\frac{ND}{l}\right). \tag{3}$$

For steel $\rho = 7\cdot85$ and since $J = 4\cdot18 \times 10^7$

$$\delta W = 0\cdot000436 q\delta\,(ND/l). \tag{4}$$

Thus in the fifth stage of twisting of the mild steel specimens of Table I, $q = 43{,}700$ lbs. per sq. in., $\delta(ND/l) = 0\cdot1452 - 0\cdot1126 = 0\cdot0326$ so that $\delta W = 0\cdot621$ calories per gram. The values of δW calculated in this way are given in column 3.

The observed rise in temperature δT is given in column 4 and the quantity of heat δH necessary to raise the metal through δT° C., namely, $\sigma\delta T$, where σ is the specific heat, is given in column 5. For steel $\sigma = 0\cdot106$ so that the figures in column 5, Table I, are derived from those of column 4 by multiplying by $0\cdot106$.

The difference between the work done on the specimen and heat given out is $\delta W - \delta H$ so that the proportion of the work done on the metal which remains latent in it is $(\delta W - \delta H)/\delta W$. This is expressed as a percentage in column 6. It will be seen that during successive stages the proportion of heat remaining latent is very nearly constant and equal to 11% of the work done on the steel. There is, however, some evidence of a slight falling off during the last stage of twisting, when the proportion of latent energy falls to 9%. In this case the total work done W is found by adding all the figures in column 3. Thus $W = 6\cdot75$ gram calories. This is equivalent to a rise in temperature of 64° C. H, the total heat emitted, is found by adding the figures in column 5. H is $5\cdot99$ calories, so that the total latent energy in the specimen at the end of the experiment is $W - H = 0\cdot76$ calories per gram, which is equivalent to a rise in temperature of $7\cdot1^\circ$ C.

The corresponding results for decarburized mild steel (nearly pure iron) are given in Table II. It will be seen, referring to the last column of the table, that there is a very definite falling off in the proportion of energy which remains latent. From 12% in the early stages it falls to about 7·5% in the last stage of the test. The energy latent in the metal at the end of the experiment was 0·67 calories per gram which is equivalent to a rise in temperature of 6·3° C.

Table I.—Mild Steel Annealed *in vacuo*. Test using Thermo-junction.

1. ND/L.	2. q. lb. per sq. in.	3. δW. cal./gm.	4. δT. ° C.	5. δH. cal./gm.	6. $\frac{\delta W - \delta H}{\delta W} \times 100$.
0·01655	14,730	0·106	0·975	0·1033	2·55
0·0455	26,200	0·331	2·76	0·292	11·76
0·0824	35,400	0·569	4·7	0·498	12·6
0·1126	39,250	0·515	4·3	0·456	11·4
0·1452	43,700	0·621	5·4	0·545	12·2
0·1768	44,250	0·606	4·98	0·528	12·85
0·2068	45,750	0·600	5·05	0·535	10·85
0·2447	47,400	0·781	6·60	0·700	10·37
0·2757	48,800	0·658	5·45	0·577	12·3
0·3052	49,100	0·632	5·25	0·556	12·0
0·3355	49,700	0·656	5·50	0·583	11·1
0·3660	50,800	0·676	5·52	0·615	9·02

W = 6·75 calories per gram. H = 5·99 calories per gram.
W − H = 0·76 calories per gram.

Table II.—Decarburized Mild Steel. Test using Thermo-junction.

1. ND/L.	2. q. lbs. per sq. in.	3. δW. cal./gm.	4. δT. ° C.	5. δH. cal./gm.	6. $\frac{\delta W - \delta H}{\delta W} \times 100$.
0·0429	16,650	0·311	2·9	0·3075	—
0·0808	26,050	0·430	3·61	0·383	13·5
0·1175	31,400	0·502	4·16	0·441	11·7
0·1537	33,850	0·534	4·42	0·469	12·1
0·1896	35,250	0·552	4·65	0·493	10·7
0·2255	36,800	0·576	5·04	0·534	7·3
0·2599	39,050	0·586	4·92	0·522	10·9
0·2940	39,700	0·590	4·90	0·520	11·9
0·3296	40,400	0·627	5·24	0·556	11·7
0·3655	41,500	0·650	5·46	0·579	12·45
0·4014	42,200	0·660	5·60	0·594	10·0
0·4369	42,200	0·654	5·70	0·605	7·5
0·4724	43,050	0·667	5·80	0·615	7·8
0·5084	43,400	0·681	5·98	0·634	6·9

W = 7·92 calories per gram. H = 7·25 calories per gram.
W − H = 0·67 calories per gram.

Heat Measurement with a Calorimeter.

The method just described has two definite defects. Firstly, it assumes that the specific heat of the specimen remains constant during the test and, secondly, there is always a certain element of uncertainty in measurements made with a thermocouple applied to the outside of a specimen. For these reasons it was decided to repeat the experiments using a calorimeter to measure δH directly. For this purpose it was necessary to reduce the loss of heat from the ends of the specimen as much as possible. This was accomplished (*a*) by making the large square section ends long so that the heat which was generated in the small diameter central part of the specimen would remain in it till the wave of temperature had penetrated down the square ends as far as the grips; (*b*) by inserting a heat-insulating material between the grips and the specimen; (*c*) by carrying out each stage of the twisting as rapidly as possible; (*d*) by re-designing the grips so that the specimen could be removed and dropped in the calorimeter within 1 second of the end of the twisting test.

By varying the time during which the specimen remained on the machine after twisting and before dropping it into the calorimeter, we were able to estimate the loss of heat and we found that when the experiment was carried out as rapidly as possible, the loss was considerably less than 1% of the heat generated. This is so small that we did not attempt to use such corrections. The rise in temperature of the water in the calorimeter was measured by means of a Beckmann thermometer.

Results.—Measurements using a calorimeter were carried out with bars made of pure copper, mild steel, and decarburized mild steel (*i.e.*, nearly pure iron). The results are given in Tables III, IV, and V. In these tables the columns 1, 2, and 3 give ND/l, q, and δW. Column 4 gives δH which is now measured directly (in Tables I and II it was found by multiplying the observed temperature rise δT by a value for the specific heat of the metal taken from physical tables). Column 5 gives the percentage of the energy used during each stage of twisting which remains latent in the specimen. Column 6 gives the total work done on the specimen expressed in calories per gram of metal. Column 7 gives the total latent energy due to twisting, expressed in calories per gram, which remains in the metal at the end of each stage of the test.

In the previous work of Farren and Taylor, it was pointed out that the proportion $(\delta W - \delta H)/\delta W$ of the work done during cold working which remains latent in the metal is nearly constant over the range covered by these experiments, though the change in the strength of the material in the same range is very great.

Table III.—Annealed Pure Copper. Test using Calorimeter.

1. ND/L.	2. q. lb. per sq. in.	3. δW. cal./gm.	4. δH. cal./gm.	5. $\frac{\delta W - \delta H}{\delta W} \times 100$.	6. W. cal./gm.	7. W − H. cal./gm.
0·0594	8,680	0·1974	0·1785	9·58	0·1974	0·0189
0·1230	14,320	0·3488	0·3235	7·25	0·5462	0·0439
0·1870	17,000	0·4168	0·3885	7·64	0·9630	0·0722
0·2670	19,550	0·5995	0·554	7·60	1·5625	0·1177
0·3598	21,690	0·7710	0·718	8·17	2·3335	0·1707
0·4195	23,250	0·5310	0·4805	9·52	2·8645	0·2212
0·4875	24,290	0·6328	0·5815	8·10	3·4973	0·2725
0·577	25,330	0·8690	0·791	8·58	4·3663	0·3505
0·642	26,380	0·6570	0·590	10·20	5·0233	0·4175
0·7035	26,900	0·6340	0·576	9·15	5·6573	0·4755
0·756	27,320	0·5495	0·490	8·58	6·2068	0·5350
0·817	27,750	0·648	0·587	9·42	6·8548	0·5960
0·876	28,200	0·637	0·584	8·32	7·4918	0·6490
0·972	28,800	1·058	0·945	10·67	8·5498	0·7620
1·067	29,160	1·062	0·965	9·08	9·6118	0·8590
1·153	30,200	0·995	0·911	8·45	10·6068	0·9430
1·253	30,350	1·162	1·066	8·25	11·7688	1·0390
1·278	30,550	0·2924	0·268	8·34	12·0612	1·0634
1·340	30,700	0·730	0·696	4·66	12·7912	1·0974
1·395	31,220	0·6578	0·634	4·19	13·4490	1·1210
1·426	31,400	0·3729	0·355	4·80	13·8219	1·1391
1·448	31,580	0·266	0·256	3·72	14·0879	1·1490

Table IV.—Annealed Mild Steel. Test using Calorimeter.

1. ND/L.	2. q. lb. per sq. in.	3. δW. cal./gm.	4. δH. cal./gm.	5. $\frac{\delta W - \delta H}{\delta W} \times 100$.	6. W. cal./gm.	7. W − H. cal./gm.
0·067	30,000	0·870	0·769	11·62	0·870	0·161
0·1353	39,200	1·158	1·070	8·23	2·028	0·189
0·201	43,800	1·240	1·117	9·92	3·268	0·312
0·267	46,650	1·336	1·209	9·51	4·604	0·439
0·3335	49,000	1·420	1·293	8·95	6·024	0·566
0·4322	51,700	2·20	2·020	8·19	8·224	0·746
0·499	52,580	1·529	1·398	8·57	9·753	0·877
0·566	53,800	1·558	1·427	8·42	11·311	1·008
0·635	54,680	1·605	1·507	6·10	12·916	1·106
0·702	55,500	1·620	1·519	6·72	14·536	1·267

It has been suggested that the latent energy due to cold work which can be retained in a metal may not increase indefinitely as the amount of cold work increases, but that a stage may ultimately be reached in which cold work can still be done on the metal, but no further latent heat can be absorbed. To show how far the present results support this view the values of $100(\delta W - \delta H)/\delta W$ given in Tables I to V are plotted against ND/l in figs. 4, 5, and 6. It will be seen from those diagrams that for annealed mild steel and decarburized mild steel the proportion of applied cold work which remains latent decreases as ND/l increases. For decarburized mild steel, fig. 5, the absorption has decreased to 2·9% of the applied work when ND/l = 0·59 and the curve seems to suggest that at the maximum observed value of ND/l, namely, 0·59, the metal has reached a state in which it is nearly saturated with latent energy. From Table II it will be seen that the total latent energy is then 0·66 calories per gram.

Table V.—Decarburized Mild Steel. Test using Calorimeter.

1. ND/L.	2. q. lb. per sq. in.	3. δW. cal./gm.	4. δH. cal./gm.	5. $\dfrac{\delta W - \delta H}{\delta W} \times 100.$	6. W. cal./gm.	7. W − H. cal./gm.
0·0625	21,300	0·5790	0·5322	8·08	0·5790	0·0468
0·1469	32,600	1·1980	1·0890	8·10	1·7770	0·1558
0·2408	36,400	1·487	1·3480	9·35	3·264	0·295
0·3220	39,550	1·398	1·280	8·44	4·662	0·413
0·4092	41,650	1·580	1·4690	7·03	6·242	0·524
0·506	42,500	1·790	1·700	5·03	8·032	0·614
0·5900	43,400	1·586	1·540	2·90	9·618	0·660

For annealed mild steel, fig. 4, the diagram indicates that at the maximum observed value of ND/l, namely, 0·70, the material is not yet saturated with latent energy, though the proportion of the applied cold work which is absorbed and remains latent is only about half what it was in the initial annealed state. When ND/l = 0·7, W − H = 1·27 calories per gram. For copper, fig. 6, shows that the proportion of the applied cold work which remains latent is nearly constant up to ND/l = 1·0, and that after this stage of the twisting has been reached the absorption of latent energy rapidly decreases till the metal becomes saturated at about ND/l = 1·6. The maximum measured value of W − H is 1·15 calories per gram at ND/l = 1·45, and fig. 6 suggests that this may be nearly the maximum possible latent energy which the metal can retain at the temperature (15° C.) at which the measurements were made.

Comparison with Measurements of Farren and Taylor.

It is not possible to compare these results directly with those of Farren and Taylor because the type of distortion was different in the two experiments, but if it be assumed that the condition of the metal depends only on the amount of applied cold work retained latent in it irrespective of the distribution of the

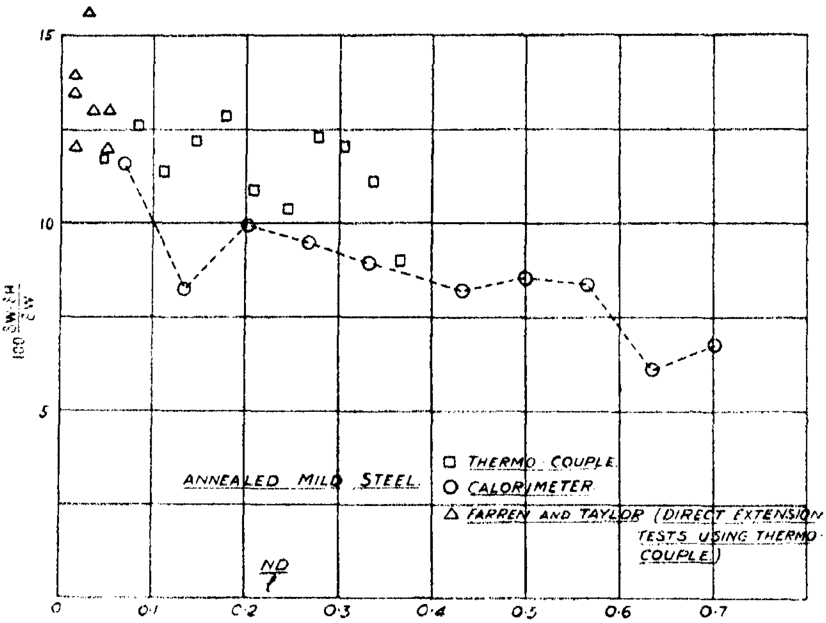

Fig. 4.

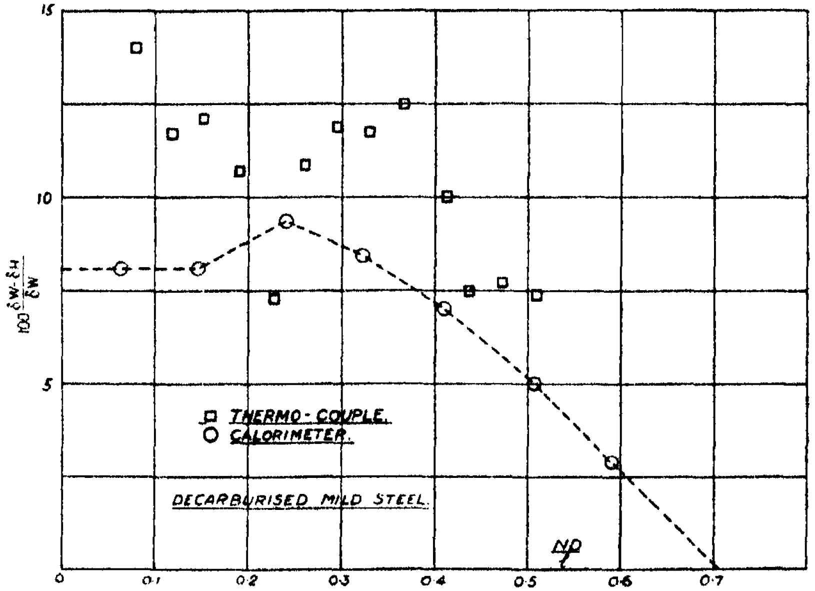

Fig. 5.

Figs. 4, 5.—Percentage of work done which remains latent in specimen subjected t plastic twisting.

applied stresses, then a virtual value of ND/l can be calculated* for which a twisted rod would have received the same amount of cold work as that given by the direct load in Farren and Taylor's experiments. The value of $100(\delta W - \delta H)/\delta W$ given by Farren and Taylor have been plotted in figs. 4 and 6 at the appropriate virtual values of ND/l. It will be seen that the agreement with the present results is good, but that a direct load is capable of giving to these metals only a very small fraction of the latent energy which they can contain.

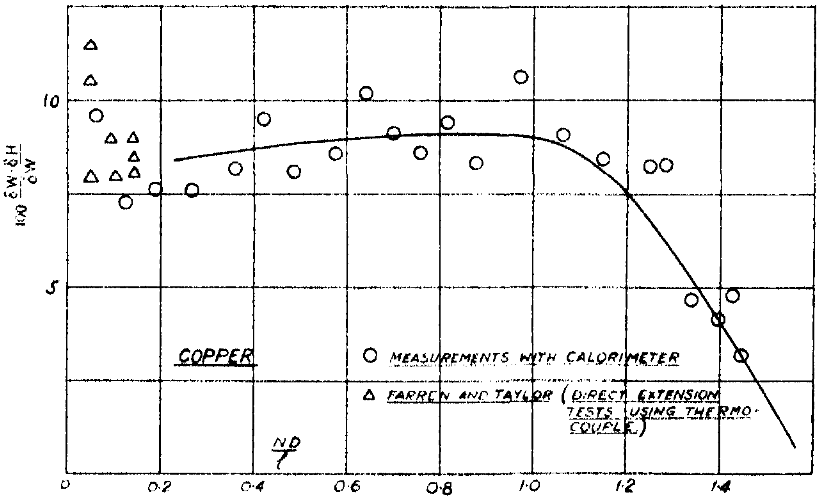

FIG. 6.—Percentage of work done which remains latent in specimen subjected to plastic twisting.

Connection between Strength and Latent Energy.

It appears that both the strength and the latent energy of the material increase with increasing amounts of cold work. For both these, however, there seems to be a limit beyond which there is no further increase with further application of cold work. The question may naturally be asked are these two limits identical? Does the attainment of maximum strength in a metal occur when the absorption of latent energy reaches its greatest possible value?

The values of q given in columns 2 of Tables I to V are mean values of the shear stress over the section. The value of the shear stress q_s at the surface of the specimen may be found from the measured values of q by means of the following formula†

$$q_s = q + \tfrac{1}{3}\frac{\text{ND}}{l}\frac{dq}{d(\text{ND}/l)}. \tag{5}$$

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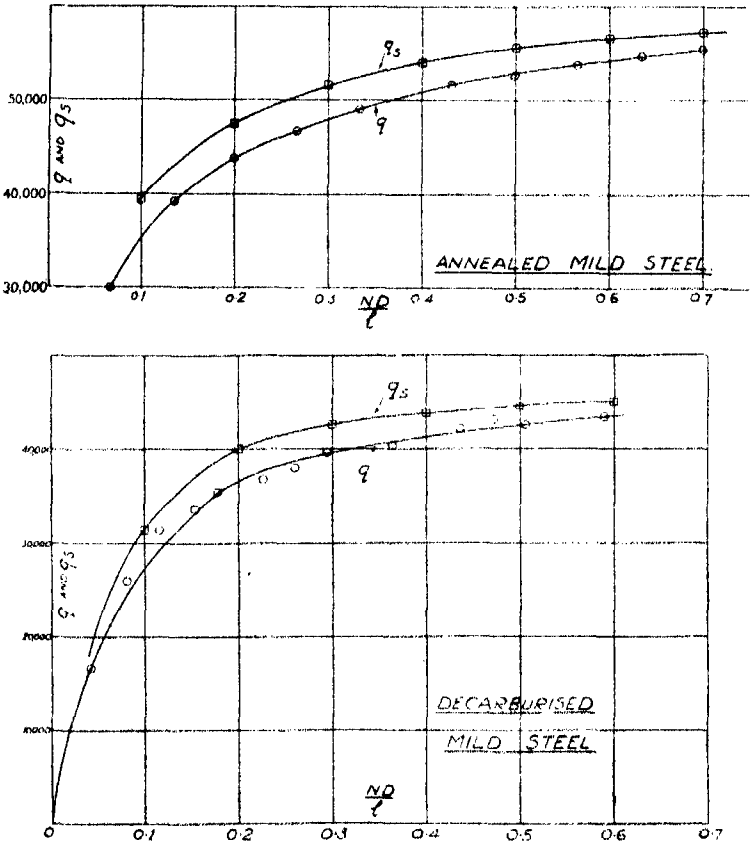
* See p. 315 above.

† This relation is given by Nadai in a different form in his "Plasticity," p. 128.

The relationship between q and ND/l for annealed mild steel and decarburized mild steel is shown in figs. 7 and 8 and the values of q_s found by applying (5) to these curves are also given in the same figure. It will be seen that for decarburized mild steel, fig. 8, q_s increases rapidly up to $\mathrm{ND}/l = 0 \cdot 4$, but that at this point the increase practically ceases. Turning to fig. 5 it will be seen that the proportion of applied cold work which becomes latent in the metal does not appear to decrease till about $\mathrm{ND}/l = 0 \cdot 4$, but that it decreases rapidly when ND/l rises above $0 \cdot 4$. For annealed mild steel, fig. 7, q_s increases up to $\mathrm{ND}/l = 0 \cdot 7$ and it will be noticed in fig. 4 that $(\delta\mathrm{W} - \delta\mathrm{H})/\delta\mathrm{W}$ does not suffer any rapid decrease in this range. There is a gradual decrease, but saturation with latent energy is only reached outside the range of our experiments.



FIGS. 7, 8.—Stress-strain curves during plastic twisting.

The values of q given in Table III for copper are the figures which must be used in calculating q_s, but they were obtained during the rapid twisting of the specimen. Copper is capable of withstanding a greater stress when the rate of deformation is large than when it is small. This effect seems to be considerably greater in twisted specimens than it is when the distortion is uniform. It is not possible, therefore, to deduce from Table III the point in the test at which the strength of the material ceases to increase with increasing cold work. For this reason independent experiments were made under conditions ensuring uniform distortion to find out how much cold work must be done on copper before it attains its maximum strength.

The Load-extension Curve for Pure Copper.

The two most convenient methods for producing uniform distortion in soft metals are to extend a long bar of uniform section or to compress a short cylinder or disc between parallel plates, the ends being lubricated with grease. The conditions under which the distortion is uniform in the latter method were studied by one of the present writers* in connection with the distortion of single crystals of aluminium. It was then found that if the load was increased only slightly between successive stages of the experiment, uniform distortion was obtained if the specimen was greased before each application of the load. The effect of the friction between the flat faces of the specimen and the parallel steel plates was found to be inappreciable.

It has been pointed out that a uniform bar extended by a direct load necessarily breaks long before the material reaches its maximum strength. A compressed disc, however, can be subjected to far greater amounts of distortion than a bar under direct load or even one subjected to torsion. In carrying out our measurements, therefore, it was necessary first to compare the curve representing T as a function of $\log (l/l_0)$ in an extension experiment with that representing P as a function of $\log (h_0/h)$ in a compression experiment. Here T and P are the stresses (expressed in lbs. per sq. in.), l is the length and l_0 the initial length of the extended bar, h is the thickness and h_0 the initial thickness of the compressed disc. If these curves are identical, it seems that the effect of the friction of the ends of the compressed disc on the steel plates is negligible and the $(P, \log h_0/h)$ curve truly represents the relationship between strength and the amount of distortion. The compression experiments can then be continued far beyond the stage at which the material reaches its maximum strength.

The results of such tests are shown in figs. 9 and 10. In the extension experiment the bar was loaded till the extension was 20%. This corresponds with $\log l/l_0 = 0{\cdot}18$ and is represented by a dotted line in figs. 9 and 10. In fig. 9 the observations in the extension experiments are represented by crosses, while those in the compression experiments are shown as round dots. It will be seen that the compression and extension curves nearly coincide so that the compression results may be used with confidence outside the range in which they can be directly compared with those obtained by tensile loading.

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* 'Proc. Roy. Soc.,' A, vol. 111, p. 531 (1926).

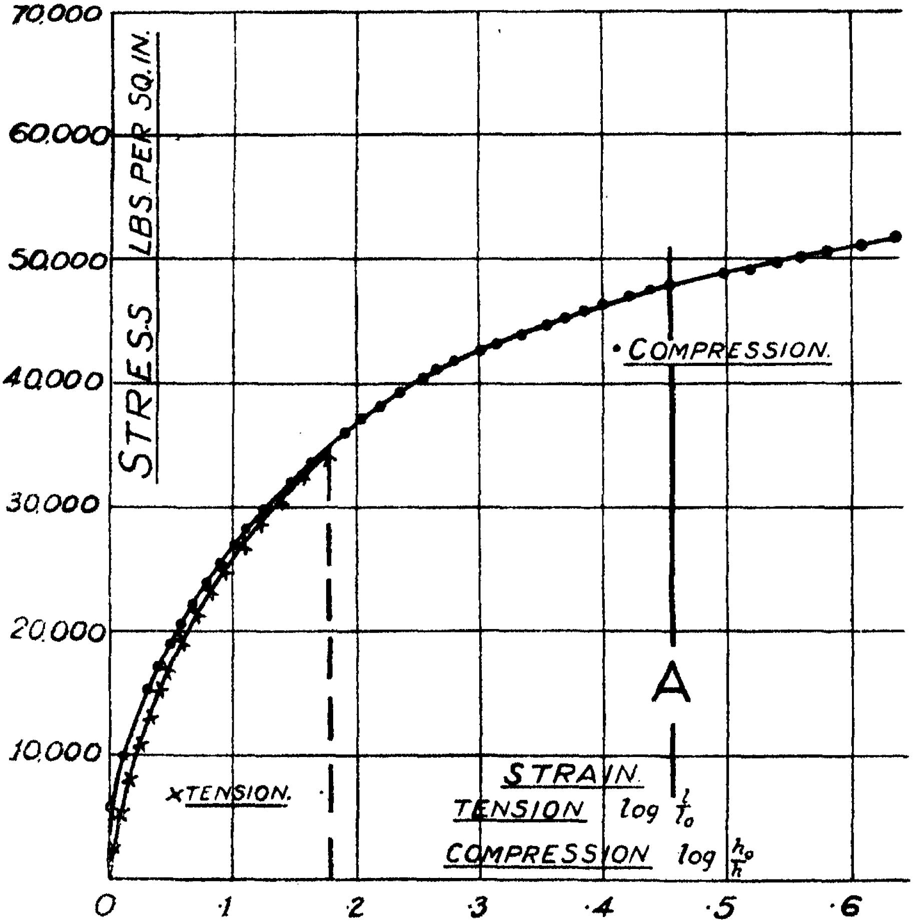

Fig. 9.—Comparison between stress-strain curves for copper in direct extension and direct compression.

The complete stress-strain curve in compression is shown in fig. 10, but for clearness only a few of the points representing the observations are marked.

A short cylinder or disc of annealed copper 0·4770 inches high × 0·4390 inches diameter was first compressed in 31 stages till its thickness was 0·61 of its original thickness. The results of this test are shown by means of 31 dots in fig. 9 and 11 dots in fig. 10. The line A at log $h_0/h = 0 \cdot 46$ marks the end of this stage of the experiment.

At this stage the specimen was 0·3007 inches thick × 0·55 inches diameter and since the effect of the friction on the ends increases as the ratio of the diameter to the thickness increases it was thought better to reduce the radius, accordingly the specimen was cut down to 0·2795 inches, the thickness remaining unaltered.

The reduced specimen was then further compressed till its thickness was 0·1178 inches. The corresponding value of log h_0/h was then 1·40. The end of this stage of the test is marked in fig. 10 by the line B. The specimen was then cut down to 0·1973 inches diameter and compressed by frequent small increments in load till its thickness was 0·0260. At the end of this third stage log $h_0/h = 2 \cdot 91$. This is indicated by the line C in fig. 10.

The remainder of the points marked in fig. 10, namely, those corresponding with strains from log $(h_0/h) = 2 \cdot 91$ to $3 \cdot 98$ were obtained with another specimen cut from the same sample of copper.

Fig. 10 shows that the compressive stress rises with increase in strain till at

$$\log(h_0/h) = 1 \cdot 5, \text{ i.e., } h/h_0 = 0 \cdot 22,$$

the maximum value of 60,000 lbs. per sq. in. is attained. No further increase was observed, although the specimen was compressed till at log $(h_0/h) = 3 \cdot 98$ its thickness was only 1/53rd of its original thickness. It is worth noticing that 60,000 lbs. per sq. in. is about equal to the tensile strength of hard drawn copper wires.

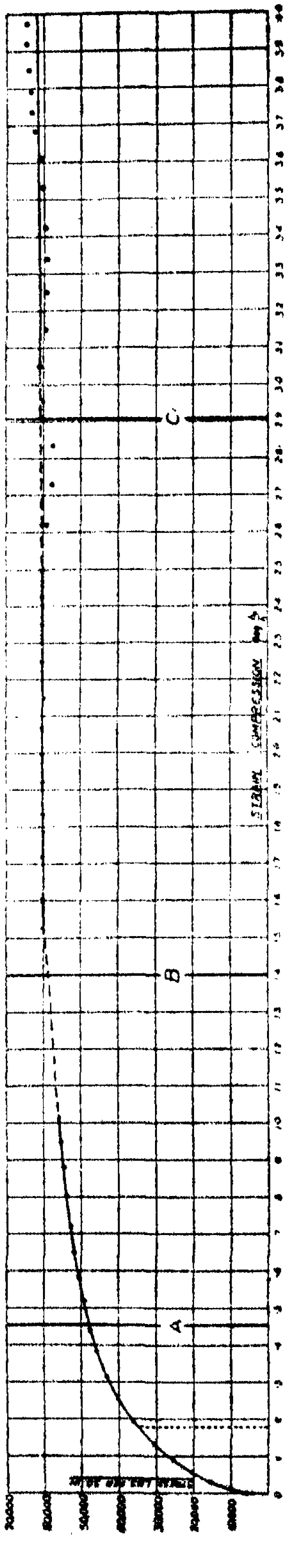

FIG. 10.—Stress-strain curve for copper in compression. At maximum strain (log $h_0/h = 3 \cdot 98$) height of specimen was 1/53rd of the original height.

Cold Work necessary to raise Strength to Maximum.

The work done on unit volume of material during compression from thickness h_0 to thickness h is

$$\int_h^{h_0} \mathrm{P}\, d\,(\log h_0/h).$$

This can be found by means of a planimeter from the curve of fig. 10. During the course of the compression to $\log h_0/h = 1\cdot5$ the work done is found in this way to be $5\cdot78 \times 10^9$ ergs. per cubic centimetre. Since the density of copper is $8\cdot93$ this is equivalent to $15\cdot5$ calories per gram of copper.

Comparison between Cold Work necessary to Saturate Metal with Latent Energy and that necessary to give Maximum Strength.

It has already been pointed out in connection with fig. 6 that the absorption of latent energy has nearly ceased at $\mathrm{ND}/l = 1\cdot45$, and from Table III it will be seen that at this stage $\mathrm{W} = 14\cdot1$ calories per gram. The cold work necessary to saturate copper with latent energy at room temperature (about 15° C.) is therefore roughly the same as that necessary to raise the metal to its maximum strength, namely, $15\cdot5$ calories per gram.

Another way in which this question might be treated is to make use of v. Mises' hypothesis concerning the criterion for plastic deformation and to assume also that the state of the material depends only on the amount of cold work done on it irrespective of whether it has been distorted by pure extension or by pure shear. Using these hypotheses s, the amount of shear equivalent to compression from thickness h_0 to thickness h is $\sqrt{3}\log(h_0/h)$, so that the maximum strength of a twisted tube would be attained when $s = \sqrt{3}(1\cdot5) = 2\cdot6$. Since $s = \pi\mathrm{ND}/l$ the maximum strength of the copper might be expected to be attained in the outer layers of a twisted copper rod when $\mathrm{ND}/l = 2\cdot6/\pi = 0\cdot83$. Using Mohr's hypothesis instead of v. Mises', the result would have been $\mathrm{ND}/l = 2\,(1\cdot5)/\pi = 0\cdot95$. It has been pointed out in discussing fig. 6 that the latent energy absorbed in twisting a copper bar bears an almost constant ratio to the applied cold work up to $\mathrm{ND}/l = 1\cdot0$, and that at that point it suddenly begins to decrease. It seems significant that this decrease occurs at a stage of twisting which so nearly coincides with that at which the maximum strength is reached in the outer layers of the specimen.

In conclusion, we wish to express our thanks to Professor Inglis for allowing us to carry out this work in the Engineering Laboratory at Cambridge, and to Mr. Parkes and Mr. Jacobsohn for assistance in carrying out the work.

The Masses of the Proton and Electron.

By Sir ARTHUR EDDINGTON, F.R.S.

(Received September 4, 1933.)

1. The conclusion reached in this paper is that the mass m of an elementary particle (proton or electron) is given by the quadratic equation

$$10m^2 - 136mm_0 + m_0^2 = 0,$$

where

$$m_0 = \frac{h}{2\pi c} \frac{\sqrt{N}}{\rho},$$

N being the number of such particles in the universe, and ρ being the radius of curvature of an empty region, equal to $\sqrt{(3/\lambda)}$ where λ is the cosmical constant.

Except for a slight difference in the definition of N and ρ, this result agrees with the formulæ suggested in preliminary papers.[†]

A review of the physical principles underlying the calculation is given in § 12. The mathematical analysis is a continuation of that developed in my earlier papers,[‡] and a general familiarity with the wave tensor calculus is assumed.

2. I have shown in earlier papers that the ordinary vectors of physics t_μ (here called *space vectors*) are connected with mixed wave tensors of the second rank T by the formula

$$T = \Sigma E_\mu t_\mu, \tag{2.1}$$

the E_μ being matrix square roots of -1 satisfying a certain scheme of commutation relations.[§] We now consider the corresponding theory of a covariant wave tensor of the second rank. We resolve it into components t_μ by the same formula (2.1), but t_μ will no longer be a space vector.

The elementary transformations of covariant and contravariant wave vectors are

$$\chi \rightarrow e^{\frac{1}{2}E_\mu\theta}\chi \qquad \chi^* \rightarrow \chi^* e^{-\frac{1}{2}E_\mu\theta}. \tag{2.2}$$

First let the matrix E_μ be antisymmetrical, so that $(E_\mu)_{\alpha\beta}\chi_\beta = -\chi_\beta(E_\mu)_{\beta\alpha}$.[‖] Hence

$$(e^{\frac{1}{2}E_\mu\theta})_{\alpha\beta}\chi_\beta = \chi_\beta(e^{-\frac{1}{2}E_\mu\theta})_{\beta\alpha}. \tag{2.3}$$

[†] 'Proc. Roy. Soc.,' A, vol. 133, p. 605; vol. 134, p. 523 (1931).

[‡] Especially 'Proc. Roy. Soc.,' A, vol. 133, p. 311 (1931).

[§] 'Proc. Roy. Soc.,' A, vol. 133, p. 312 (1931).

[‖] We adopt the summation convention for row-and-column suffixes, but not for any other suffixes.

Comparing (2.2) and (2.3) we see that there is no difference between the transformations of χ and χ^*, and consequently no difference between the transformations of covariant and mixed wave tensors. For clearness we prove the last result directly for a covariant wave tensor $T_{\alpha\beta}$

$$
\begin{aligned}
T_{\alpha\beta} \rightarrow & \, (e^{\frac{1}{2}E_\mu\theta})_{\alpha\gamma} \, (e^{\frac{1}{2}E_\mu\theta})_{\beta\delta} \, T_{\gamma\delta} \\
= & \, (e^{\frac{1}{2}E_\mu\theta})_{\alpha\gamma} \, (e^{-\frac{1}{2}E_\mu\theta})_{\delta\beta} \, T_{\gamma\delta}, \qquad \text{since } E_\mu \text{ is antisymmetrical} \\
= & \, (e^{\frac{1}{2}E_\mu\theta})_{\alpha\gamma} \, T_{\gamma\delta} \, (e^{-\frac{1}{2}E_\mu\theta})_{\delta\beta} \\
= & \, (e^{\frac{1}{2}E_\mu\theta} \, T e^{-\frac{1}{2}E_\mu\theta})_{\alpha\beta},
\end{aligned}
\tag{2.4}
$$

which is the law of transformation of a mixed wave tensor.

If E_μ is symmetrical we have similarly

$$T_{\alpha\beta} \rightarrow (e^{\frac{1}{2}E_\mu\theta} \, T e^{\frac{1}{2}E_\mu\theta})_{\alpha\beta}. \tag{2.5}$$

This transformation is called in my earlier papers an *antiperpendicular rotation* or *strain*.[†]

I shall call the components t_μ of a covariant wave tensor a *strain vector*. Accordingly a strain vector behaves like a space vector when E_μ is antisymmetrical, but substitutes antiperpendicular rotations for ordinary rotations when E_μ is symmetrical.

Since space vectors and strain vectors have 16 components we picture them in a space of 16 dimensions. Let OP, OQ represent a space vector and a strain vector respectively, and at first let OQ coincide with OP. Now perform the infinitesimal transformation

$$\chi \rightarrow e^{\frac{1}{2}\Theta}\chi, \qquad \chi^* \rightarrow \chi^* e^{-\frac{1}{2}\Theta}, \tag{2.6}$$

which gives a rotation of the axes in 16 dimensions, Θ being a general infinitesimal fourfold matrix. The antisymmetrical part of Θ changes space vectors and strain vectors equally; the symmetrical part transforms them differently and so produces a relative displacement PQ.[‡] Since the symmetrical part contains 10 independent elements, PQ describes a 10-dimensional space. The point P is a fixed origin, because OP (being a vector in the ordinary sense) remains geometrically fixed whilst its components are changed by the rotation of the axes of reference. In our physical applications the locus of Q will be identified with the phase space of a system described by simple wave vectors.

It simplifies our analysis to employ a frame of four-point matrices. In that case the antisymmetrical matrices E_μ are real and the symmetrical matrices are imaginary. The corresponding transformations are therefore related like time-like and space-like displacements. I shall therefore call transformations and components corresponding to real (antisymmetrical) E_μ *time-like*, and the others *space-like*. Space and time cannot be interchanged in this identification because it is necessary to provide three mutually perpendicular directions of space-like transformation and this cannot be managed with real E_μ.

[†] 'Proc. Roy. Soc.,' A, vol. 138, pp. 20, 22 (1932).

[‡] It can be proved that the displacement does not vanish, provided that OQ is non-singular, *i.e.*, provided it has a reciprocal.

Similar results hold for double wave vectors (with two suffixes). The double wave tensor of the second rank, *e.g.*, $T_{\alpha\beta,\gamma\delta} = \Psi'_{\alpha\beta}\Phi_{\gamma\delta}$, is resolved into 256 components $t_{\mu\nu}$ by the formula

$$T_{\alpha\beta,\gamma\delta} = \sum_{\mu,\nu} (E_\mu)_{\alpha\gamma} (F_\nu)_{\beta\delta}\, t_{\mu\nu}. \tag{2.7}$$

Here F_ν is the same matrix as E_ν; it is written differently in order to allow the suffixes α, β, γ, δ to be dropped in simple formulæ, the rule then being that E connects with the first suffixes and F with the second suffixes of the double vectors. The elementary transformations of covariant and contravariant double vectors are†

$$\Psi' \rightarrow e^{\frac{1}{2}E_\mu F_\nu \theta}\Psi', \qquad \Psi'^{*} \rightarrow \Psi'^{*} e^{-\frac{1}{2}E_\mu F_\nu \theta}. \tag{2.8}$$

The two transformations are the same if $E_\mu F_\nu$ is the product of a symmetrical and an antisymmetrical matrix and therefore imaginary; by analogy with the simple vectors this is defined as time-like displacement. When $E_\mu F_\nu$ is real the double strain vector undergoes antiperpendicular rotations instead of ordinary rotations.

Note that a space-like displacement corresponds to E_μ imaginary or to $E_\mu F_\nu$ real. This is because $E_\mu{}^2 = -1$, $(E_\mu F_\nu)^2 = +1$, so that the eigen values of E_μ and $E_\mu F_\nu$ are respectively imaginary and real. We may thus in all cases define space-like displacement as one whose matrix has the same real or imaginary character as its eigen value, or equivalently as one which discriminates between strain vectors and space vectors and therefore corresponds to a displacement in phase space.

Since there are 6 real and 10 imaginary E_μ, there are 136 real and 120 imaginary $E_\mu F_\nu$. Hence the phase space of a system represented by double wave vectors has 136 dimensions.

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† A "double vector" differs from a tensor of the second rank in having a transformation scheme with 256 instead of 16 coefficients. The most general transformation of a tensor $T_{\alpha\beta}$ of the second rank is $T'_{\alpha\beta} = a_{\alpha\gamma}a_{\beta\delta}T_{\gamma\delta}$; the most general transformation of a double vector $\Psi_{\alpha\beta}$ is $\Psi'_{\alpha\beta} = a_{\alpha\beta\gamma\delta}\,\Psi_{\gamma\delta}$.

3. It is a feature of statistical mechanics that phase space is space in the ordinary sense, not space-time. The whole probability is given by integration of its elements over a spatial domain; there is no integration with respect to time. The necessity for eliminating time-like dimensions seems to compel us to describe configurations in phase space by strain vectors and not by ordinary vectors. We may say that, although all kinds of tensors may be used in the description of phenomena, it is only the strain vectors which can supply a field of application for statistical mechanics. This condition has caused quantum mechanics to develop in a direction rather away from relativity, for the more elementary relativistic properties of a system are most obvious when it is described in terms of space vectors.

The 10-dimensional locus of Q is selected as phase space for the following reasons:—

(*a*) It is derived from wave vectors of Dirac's type which are understood to describe electrons or protons.

(*b*) It has a structure describable by a group of operations.

(*c*) All displacements in it are space-like.

Taking an arbitrary point Q in the phase space as origin, let Θ be the matrix of the transformation (2.6) which displaces Q to Q′. Let $\Theta = \Sigma E_\mu \theta_\mu$. Then θ_μ forms locally a natural co-ordinate system for describing configurations Q′ in the neighbourhood of Q. We call this the *local orthogonal co-ordinate system*. Difficulties of non-commutation arise if the squares of θ_μ are not negligible; so for the present we restrict these co-ordinates to an infinitesimal range (see § 4).

In dealing with a small region it is simplest to take OQ along the algebraic axis x_{16} so that the strain vector at the origin is algebraic,† say, $T = R$, or $T_{\alpha\beta} = R\,(1)_{\alpha\beta}$. A neighbouring configuration with co-ordinates θ_μ will then have the strain vector

$$T' = (e^{\frac{1}{2}\Sigma E_\mu \theta_\mu})_{\alpha\gamma}\,(e^{\frac{1}{2}\Sigma E_\mu \theta_\mu})_{\beta\delta}\,(1)_{\gamma\delta}\,.\,R.$$

Reducing this as in § 2, we obtain

$$T' = Re^{\Sigma' E_\mu \theta_\mu}, \tag{3.1}$$

the accent in Σ' indicating that the sum is limited to space-like components.

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† An algebraic *space vector* $E_{16}t_{16}$ is invariant. Thus we have the advantage that the comparison point P is not only geometrically fixed, but its analytical expression is fixed.

Similar considerations apply to the 136-dimensional phase space of a double strain vector. The strain vector corresponding to a point $\theta_{\mu\nu}$ in local orthogonal co-ordinates is

$$\mathrm{T}' = \mathrm{R}e^{\Sigma' \mathrm{E}_\mu \mathrm{F}_\nu \theta_{\mu\nu}},$$

the summation including only those values of μ, ν for which $\mathrm{E}_\mu \mathrm{F}_\nu$ is real.

When we consider wave vectors χ or Ψ the phase space appears as a section of a space-time, since their transformations introduce time-like co-ordinates.

4. The local co-ordinate system θ_μ is inadequate when it is necessary to take account of squares of θ_μ, as in forming differential equations of the second order. Geometrically the θ_μ are not linear displacements but rotations, and they compound non-commutatively. The most suitable system of finite co-ordinates is *stereographic co-ordinates*. On a hypersphere of radius R the stereographic co-ordinates are such that the line element is

$$ds^2 = -(1 + r^2/4\mathrm{R}^2)^{-2}(dx^2 + dy^2 + dz^2 + \dots), \tag{4.1}$$

where $r^2 = x^2 + y^2 + z^2 + \dots$. The co-ordinates are thus locally orthogonal and isotropic; but the actual length ds is λ_r times the Euclidean length, where

$$\lambda_r = (1 + r^2/4\mathrm{R}^2)^{-1}. \tag{4.2}$$

Spherical space is in this way projected into a Euclidean space with a variable gauge-factor.

The corresponding co-ordinates in our phase space are defined as follows: We write $\mathrm{X} = \Sigma\, \mathrm{E}_\mu x_\mu$; then stereographic co-ordinates x_μ are such that displacement from the origin to the point x_μ corresponds to the transformation

$$\chi \rightarrow \left\{\frac{1 + \mathrm{X}/2\mathrm{R}}{1 - \mathrm{X}/2\mathrm{R}}\right\}^{\frac{1}{2}} \chi. \tag{4.3}$$

I shall confine myself to a region in which X^2 is algebraic (together with its infinitesimal neighbourhood in all directions) and set

$$\mathrm{X}^2 = -r^2, \tag{4.4}$$

because it is only then that these co-ordinates closely resemble stereographic co-ordinates on a sphere. We shall not require $(\mathrm{X} + d\mathrm{X})^2$ to be algebraic.

If displacement from x_μ to $x_\mu + dx_\mu$ corresponds to $\chi \rightarrow e^{\frac{1}{2}d\Theta}\chi$, we have by (4.3)

$$e^{\frac{1}{2}d\Theta} \left\{\frac{1 + \mathrm{X}/2\mathrm{R}}{1 - \mathrm{X}/2\mathrm{R}}\right\}^{\frac{1}{2}} = \left\{\frac{1 + (\mathrm{X} + d\mathrm{X})/2\mathrm{R}}{1 - (\mathrm{X} + d\mathrm{X})/2\mathrm{R}}\right\}^{\frac{1}{2}}. \tag{4.5}$$

When X^2 is algebraic, the most general matrix $d\mathrm{X}$ can be divided into two parts, one of which commutes and the other anticommutes with X.[†] Further, the transformations corresponding to these two parts are additive, since they are infinitesimal.

First let dX commute with X; then (4·5) can be solved as an ordinary algebraic equation, giving

$$d\Theta = d\left\{\log\frac{1+X/2R}{1-X/2R}\right\} = (1 - X^2/4R^2)^{-1}\,dX/R$$
$$= (1 + r^2/4R^2)^{-1}\,dX/R. \qquad (4.6)$$

Next let dX anticommute with X; then the differential of any even power of X is zero. Since

$$\left\{\frac{1+X/2R}{1-X/2R}\right\}^{\frac{1}{2}} = \frac{1+X/2R}{(1-X^2/4R^2)^{\frac{1}{2}}},$$
$$d\left\{\frac{1+X/2R}{1-X/2R}\right\}^{\frac{1}{2}} = \frac{dX/2R}{(1-X^2/4R^2)^{\frac{1}{2}}} = \frac{dX}{2R}\left(1+\frac{X}{2R}\right)^{-1}\left\{\frac{1+X/2R}{1-X/2R}\right\}^{\frac{1}{2}}.$$

Hence, by (4.5),

$$d\Theta = (dX/R)(1+X/2R)^{-1} = (1+r^2/4R^2)^{-1}(dX/R)(1-X/2R). \qquad (4.7)$$

If X and dX are space-like and anticommute, XdX is time-like.[‡] Hence the space-like part of $d\Theta$, which is all that concerns us in the definition of phase space, is the same in (4.6) and (4.7); so that (4.6) is the general formula connecting local orthogonal co-ordinates θ_μ with the differentials of stereographic co-ordinates x_μ. We see that they agree except that there is a variable scale-factor $(1 + r^2/4R^2)^{-1}$ just as in (4.2).

The most general form of X that is here allowed is a pentadic expression $X = E_1x_1 + E_2x_2 + E_3x_3 + E_4x_4 + E_5x_5$; but we have limited X to space-like components, so that stereographic co-ordinates are limited to a space of three dimensions at the most. But the important point is that they apply also to an infinitesimal domain of the full 10 dimensions around each point, so that they can be used for treating *the finite displacement of a volume element.* The stereographic co-ordinates in (4.1) were in one respect more general because time-like displacements could be included; but there it is implied that dX is restricted to the same domain as X, so that $(X + dX)^2$ is algebraic as well as X^2.

[†] This follows because a complete set of fourfold matrices E_μ can be constructed so as to contain X/r as one of its members. [*Added Nov.* 18.—It is necessary to exclude domains of X which contain antiperpendicular dimensions. I had thought that these were excluded by the condition that X^2 is algebraic, but that is not quite a sufficient condition.]

[‡] This is true both for simple and for double wave vectors. The proof is straightforward.

The foregoing results apply to double vectors as well as simple vectors.

5. The most elementary *physical* conception is that of a magnitude expressing a relation between two parts of a system. The two " parts " are abstractions. Since all observables arise out of relations there can be no physical magnitude associated with one relatum alone. But this abstraction is the basis of our ordinary conceptions and vocabulary and of the current methods of physics. Thus the most elementary *abstract* conception is that of an indivisible part of a physical system; mathematically this is itself regarded as a system. We have to examine the process of abstraction by which in current physics simple indivisible systems are introduced as parts of combined systems, and physical magnitudes (which can only arise out of relations) are conventionally assigned to a simple system containing in itself no relations.

The difference of starting point of observational physics and abstract analysis is illustrated in the ordinary theory of space-time, the most elementary physical conception being the interval and the most elementary abstract conception being the point event.

Since the most elementary system containing anything observable must have at least two parts it cannot be described by a simple wave vector. Thus our natural starting point is a system represented by a double wave vector Ψ. This is analysed into the product (or sum of products) of two simple wave vectors ψ, χ; and the abstract concept of simple systems corresponding to the two factors is then introduced. The two parts are considered to be non-interacting for the interaction would virtually constitute a third part.†

For *discrete* wave vectors the dissection is accordingly

$$\Psi_{\alpha\beta} = \psi_\alpha \chi_\beta, \tag{5.1}$$

where Ψ represents an elementary state of the combined system S_{12}, and ψ, χ represent the corresponding elementary states of the simple systems S_1, S_2 into which we dissect it. It follows that the double strain vector T_{12} of the system S_{12} is the outer product $T_1 T_2$ of the strain vectors representing S_1, S_2.

Actually, however, the wave vectors have a continuous distribution, and the dissection (5.1) will be invalid unless the volume of the element of phase space of S_{12} is always proportional to the product of the corresponding volume elements of the phase spaces of S_1 and S_2—in short, unless Ψ and $\psi\chi$ are referred to the same basis of statistics. This would, of course, be satisfied if the three phase spaces had uniform Euclidean metric; but we have seen in § 4 that they have a structure equivalent to that of a Euclidean space with a variable gauge factor λ_r. The apparent Euclidean volume is therefore to be multiplied by a gauge factor λ_r^n, where n is the number of dimensions of the phase space.† It is therefore a necessary condition for the validity of (5.1) that at all points to which it is applied the gauge factor for the combined system shall be the product of the gauge factors for the separate systems. We shall see that this condition determines the masses of the simplest systems which result from such dissection, viz., the electron and proton.

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† According to my theory the apparent interaction of two systems arises because we inadvertently adopt a different basis of statistics in passing from the two separate systems to the combined system.

I would emphasize that, whether or not I have here succeeded in formulating correctly the condition to be satisfied by the gauge factors, there must certainly be a condition of this kind and it must give an equation of fundamental importance. It has not been noticed hitherto because quantum theory, whilst professedly attaching great importance to the distinction of "observables" and "unobservables," has ignored the most elementary requirement that an observable must correspond to a relation and therefore can only arise in a double wave system. *We must not change the basis of statistics—the co-called* a priori *probability—when we dissect the statistics of a combined system into statistics of its separate parts.* I have already pointed out that when we dissect a system consisting of a pair of electric charges into two separate charges we change the basis of statistics (because we lose the interchangeability) and thereby introduce the apparent interaction called the electromagnetic force between the charges.‡ Here the same principle is applied to a different problem—to separate off a simple wave vector from the standard comparison system, viz., physical space, without changing the basis of statistics in the separation.

6. We can specify the configurations of a system either by the components t_μ of the strain vector T or by the stereographic co-ordinates x_μ which are components of X. It is convenient to make the two representations coalesce in scale at the origin. For small values of X the angle Θ of the corresponding transformation is $d\mathrm{X}/\mathrm{R}$ by (4.6); hence if we take T = R at the origin, the strain vector at a neighbouring point is

$$\mathrm{T} = e^{\Theta}\mathrm{R} = (1 + \mathrm{X}/\mathrm{R})\mathrm{R} = \mathrm{R} + \mathrm{X} \qquad (6.1)$$

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† λ_r^n is the "weight function" (Dirac, "Quantum Mechanics," p. 69).

‡ 'Proc. Roy. Soc.,' A, vol. 122, p. 359 (1929); vol. 138, p. 17 (1932).

by (3.1). Thus, apart from an additive constant R, the representations T and X coincide near the origin.

We therefore take in our three systems

$$\mathrm{T}_1 = \mathrm{R}_1, \qquad \mathrm{T}_2 = \mathrm{R}_2, \qquad \mathrm{T}_{12} = \mathrm{R}_{12} = 1, \tag{6.2}$$

at the origin. We take T_{12} as our unit of measure because S_{12} is the system which is the subject of observation, S_1, S_2 being the result of abstract dissection. The idea is that starting from a standard configuration the processes of changing it to other configurations (including dissection into two parts) form a group which can be represented by any group of mathematical operators that has the same structure ; the original configuration is then represented by the identical operator 1. Since T_{12} is the product of T_1, T_2

$$\mathrm{T}_1\mathrm{T}_2 = \mathrm{R}_1\mathrm{R}_2 = 1,$$

so that we may write

$$\mathrm{R}_1 = q, \qquad \mathrm{R}_2 = 1/q, \qquad \mathrm{R}_{12} = 1. \tag{6.3}$$

Thus in dissecting S_{12} there is an elasticity in choosing the relative scale of the two parts provided by the arbitrary constant q ; but we shall see later that q is fixed by the condition discussed in § 5.

When in our abstract analysis two parts of a system are said to be on the same scale or on different scales, what standard of comparison common to the two parts is implied ? There can be no *direct* comparison of spatial displacements, because these are strains and cannot be divorced from the entity which suffers the strain. The common standard is displacement in time. It is an essential part of our conception of the dissection of S_{12} that when S_{12} is carried forward a second in time the two parts S_1, S_2 are also carried forward a second in time. To bring in time displacements we revert to the wave vectors $\Psi = \psi\chi$. For ψ and χ time displacement can be compared with space displacement (allowing for the factor i), by means of the Lorentz transformation.† Thus, through the intermediary of their common time displacement, space displacements in S_1, S_2 are compared indirectly.

Take a displacement X in a time-direction, say

$$\mathrm{X} = \mathrm{E}_{45}ct.$$

Since for small values of X, $\Theta = \mathrm{X}/\mathrm{R}$, the corresponding transformation of the wave vector is

$$\psi(t) = e^{\frac{1}{2}\mathrm{E}_{45}ct/\mathrm{R}}\,\psi(0). \tag{6.4}$$

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† This requires that the same divisor R converts X into angle whether X is time-like or space-like.

We obtain a wave propagated in the E_{45} direction we select that part of the distribution of ψ which is an eigen vector of E_{45}; so that in (6.4) E_{45} is replaced by its eigen value i. Then we have

$$\psi(t) = e^{ict/2R}\,\psi(0). \tag{6.5}$$

The other parts of the distribution of ψ give waves propagated in inclined directions. By the usual formula the proper mass of the particle represented by (6.5) is

$$m = \frac{h}{2\pi c}\cdot\frac{1}{2R}. \tag{6.6}$$

Thus the constants R_1, R_2 are proportional to the wave-lengths and inversely proportional to the proper masses, m_1, m_2 of the corresponding parts of the system.

At first sight it would seem that the mass of S_{12} should be $h/4\pi cR_{12}$ and therefore proportional to m_1m_2; but the mass of a combined system is not defined in that way. Mass can only be measured in terms of a comparison mass, and the foregoing treatment shows how the mass of S_1 is compared with that of a comparison system S_2 used as standard mass in the experiment. The determination of the mass of the combined system S_{12} involves the analysis of a different experiment in which it is compared with an extraneous standard S_3: and the double wave vector to be dissected represents a combination of S_{12} with S_3. A composite system has waves representing its internal and external relations respectively, and it is the wave-length of the external waves which defines the mass of the system.

7. We have now to consider what is the second system presupposed in current quantum theory when we abstract a simple wave vector to represent a proton or electron and attribute to it a mass m_1, it being remembered that unless a second physical system is conceived to be present no observable relations exist and the equations are utterly meaningless.

The second system furnishes the comparison mass m_2 or equivalently a comparison standard of length given by the corresponding wave-length. Since that is the only characteristic conceived to be potentially variable, we take S_2 to be characterized by a single parameter so that its phase space is unidimensional. The single dimension corresponds to algebraic transformations $E_{16}\theta_{16}$ which, if real, simply change the scale.

The reason why S_2 has fewer degrees of freedom than S_1 is that both in theory and in practice S_2 is a macroscopic system simplified by averaging. When we state the mass of an electron we are not comparing it with a system "like an electron " but on a different scale; we compare it with a gram weight whose mass is an averaged characteristic. Mechanical properties correspond to an algebraic Schrödinger wave function; Dirac's matrices are only introduced by the properties of electromagnetic systems.

Instead of tackling directly the theoretical analysis of an ideal experiment in which the mass of an electron is compared with that of a gram weight we introduce macroscopic space-time as an intermediary. There are then two ideal experiments. In the first the gram weight is compared with the metrical standard contained in space-time. This, being a macroscopic problem, is fully treated in the general theory of relativity. We are now discussing the second ideal experiment in which this metrical standard, embodied in the system now called S_2, is compared with the wave-length of the electron. Clearly S_2 must be identified with macroscopic space-time (or rather with its physical essence); otherwise we fail to establish connection between microscopic and macroscopic magnitudes. Space-time (so long as it has curvature) possesses mass and momentum and is therefore a genuine physical system; it is an idealized replacement of the material universe, preserving the physical properties of the latter so far as they affect a particle located in the universe and therefore in the space-time which replaces it. Its physical nature, however, resides in its curvatures, the co-ordinate lines that we draw in it being a non-physical addition. If space-time is uniform (as contemplated in the elementary equations of quantum theory which take no account of gravitational fields), it is characterized by one magnitude or scale-constant, viz., the radius of curvature.

Let the double strain vector of the system S_{12} be

$$\Psi_{\alpha\beta}\,\Phi_{\gamma\delta} = \psi_\alpha\chi_\beta \cdot \phi_\gamma\omega_\delta.$$

The dissection consists in associating ψ, ϕ with S_1 and χ, ω with S_2. But since S_2 is in practice a macroscopic average we are concerned only with a single algebraic magnitude derivable from $\chi\omega$. To form such an algebraic magnitude we must take the quarter spur or algebraic component $E_{16}t_{16}$ of the strain vector $T = \chi\omega$; or equivalently we take the inner product $\chi_\beta\omega_\beta$. The substitution of a macroscopic for a microscopic comparison system is thus equivalent to performing a contraction of suffixes.

We can now restate the theory as follows: An electron or proton is usually described by two simple wave functions ψ, ϕ. We must suppose, however, that in addition to the suffix explicitly recognized they have a second suffix referring to the physical comparison system which is always implied. But ψ

and ϕ are not observed separately; they are used to give the expectation values of certain operators, such values being always of the form $\psi S \phi$. Further, the operator S refers to some change of state of the electron, not of the comparison system, so that it does not interact with the second suffix. Therefore when the comparison system is macroscopic, we may perform the contraction of the suffix or macroscopic averaging before the operation instead of after. We may accordingly look on this contraction as an automatic effect of multiplication (*cf.* the rule of multiplication of matrices), viz.,

$$\Psi \Phi \equiv \Psi_{\alpha\epsilon} \Phi_{\beta\epsilon} = \psi_\alpha \phi_\beta \cdot \chi_\epsilon \omega_\epsilon .$$

If we were dealing with space vectors Φ would be contravariant, and the factor $\chi_\epsilon \omega^\epsilon$ would be invariant; but since we are concerned with strain vectors, $\chi_\epsilon \omega_\epsilon$ though algebraic is not invariant and constitutes a scale factor alterable by the transformations considered. This is the proper role of the system S_2 since any change of scale of the comparison system must affect quantities measured by comparison with it.

The error of the elementary theory is that it assumes that length measured in terms of a constant standard of length is an "observable"; actually the observed length is measured in terms of the extension of another physical system whose scale in terms of the assumed constant standard can only be given as a probability distribution.

8. The dissection $S_{12} \rightarrow S_1 S_2$ is accordingly expressed by

$$\psi_\alpha \chi_\beta \phi_\gamma \omega_\delta \rightarrow \psi_\alpha \phi_\gamma \cdot \chi_\beta \omega_\beta . \tag{8.1}$$

We have to apply to this the condition for the equivalence of volume elements explained in § 5. The numbers of dimensions of the phase spaces of the 4-suffixed, 2-suffixed, and 0-suffixed expressions in (8.1) are respectively

$$n_{12} = 136, \qquad n_1 = 10, \qquad n_2 = 1. \tag{8.2}$$

We consider an algebraic displacement X in all three phase spaces.[†] This would be written

$$X = E_{16} r, \qquad X = F_{16} r, \qquad X = E_{16} F_{16} (r/i),$$

according to the phase space considered; the three expressions are equivalent since $E_{16} = F_{16} = i$. By § 4 this introduces a gauge-factor $(1 + r^2/4R^2)^{-1}$ for a length, or $(1 + r^2/4R^2)^{-n}$ for an n-dimensional volume element. Hence the condition is

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[†] For the reason why an algebraic displacement (like a time displacement) is common to all three systems, see § 13.

$$\left(1 + \frac{r^2}{4R_{12}}\right)^{-n_{12}} = \left(1 + \frac{r^2}{4R_1^2}\right)^{-n_1}\left(1 + \frac{r^2}{4R_2^2}\right)^{-n_2}. \qquad (8.3)$$

Hence, expanding as far as r^2 and using (6.3)

$$-n_{12} = -n_1/q^2 - n_2 q^2,$$

or, since $q^2 = R_1/R_2 = m_2/m_1$ by (6.6)

$$n_1 m_1^2 - n_{12} m_1 m_2 + n_2 m_2^2 = 0. \qquad (8.4)$$

Finally by (8.2)

$$10 m_1^2 - 136 m_1 m_2 + m_2^2 = 0. \qquad (8.5)$$

The condition (8.3) is only satisfied as far as r^2, but this is sufficient to determine m_1, m_2 as coefficients in a second order differential equation. As this is the way m_1, m_2 are used in physics it is the appropriate identification.†

Equation (8.5) gives two values of m_1 which are in the ratio 1847·6 and correspond to protons and electrons respectively. I have shown elsewhere that the two roots ordinarily represent charges of equal and opposite sign.‡

The asymmetry of (8.5) is due to the fact that it connects a unit m_1 of microscopic structure with a unit m_2 of macroscopic structure of the universe.

If we take X to be a non-algebraic displacement there is no longer any direct correspondence of displacements in the three phase spaces. The condition of equivalence of volume elements still holds, but it now determines the displacement X_{12} in the space of S_{12} which must (for consistency) be taken to correspond to a given displacement X_1, say $X_1 = E_1 r$, in the space of S_1. Since S_2 can only take part in algebraic transformations (change of scale) the corresponding displacement of S_2 is assumed to be zero. The condition now becomes

$$\left(1 - \frac{X_{12}^2}{4R_{12}^2}\right)^{-136} = \left(1 - \frac{X_1^2}{4R_1^2}\right)^{-10}, \qquad (8.6)$$

which gives by (6.3)

$$136 X_{12}^2 = 10 X_1^2/q^2.$$

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† Stereographic co-ordinates are an arbitrary system used to simplify this particular investigation. We must not attempt to get out of them more than could be obtained from any other system of co-ordinates in space of the same uniform curvature, viz., a second order differential equation determining R or its reciprocal m.

‡ 'Proc. Roy. Soc.,' A, vol. 134, p. 530 (1931). The discovery of the positive electron may seem to contradict this; but, so far as it has been observed, the conditions of its occurrence are certainly not those of statistical equilibrium contemplated in the elementary equations of quantum theory.

By (8.5)

$$136/10 = (m_1 + m'_1)/m_2,$$

where m_1, m'_1 are the two roots of the quadratic. Hence

$$\frac{X_1^2}{X_{12}^2} = \frac{m_1 + m'_1}{m_1}. \tag{8.7}$$

It follows that the Hamiltonian

$$\frac{1}{2m_1} \Sigma \left(\frac{ih}{2\pi} \frac{\partial}{\partial x_1}\right)^2 = \frac{1}{2\,(m_1 + m'_1)} \Sigma \left(\frac{ih}{2\pi} \frac{\partial}{\partial x_{12}}\right)^2. \tag{8.8}$$

9. The macroscopic comparison system S_2 represents the mean of a great number of particles, say N. These are replaced by N elementary wave systems each in its own fixed direction, but covering all directions equally. That is to say, instead of assigning to each particle equal probability of momentum in any direction we assign the average number of particles to each small range of direction of the momentum vector. This eliminates changes which merely permute the particles and are not recognizable macroscopically.

Each wave system, being in a fixed direction, has one potentially variable characteristic, viz., its wave-length or scale. The combined phase space of the N systems each with *one* variable has been replaced by the unidimensional phase space of S_2. The condition of equivalence of volume elements for an algebraic displacement X gives

$$\left(1 - \frac{X^2}{4R_2^2}\right)^{-1} = \left(1 - \frac{X^2}{4\rho^2}\right)^{-N}, \tag{9.1}$$

where ρ is the radius for converting X into angle in the phase space of a single wave system, so that the wave vector of one of the N elementary waves is

$$\psi = e^{iX/\rho}\, \psi_0. \tag{9.2}$$

Expanding (9.1) we have

$$1/R_2^2 = N/\rho^2. \tag{9.3}$$

This is also obvious from the fact that the probability distribution of the mean of N independent particles is on a scale $1/\sqrt{N}$ times the scale of the probability distribution of a single particle.

We shall first take the comparison system to be the whole universe. This is in order to avoid the complication of introducing conditions which limit S_1 to a particular part of the universe. Then N is the whole number of particles in the universe, believed to be of order 10^{79}. By (9.3) ρ is enormously larger than R_2 and is, in fact, of cosmical magnitude. It therefore suggests itself that the change of ψ in (9.2) is the relativity transformation due to the rotation of the axes of reference in following the curvature of the world. In other words, the phase space of the elementary wave system is actual space, and its radius of curvature ρ is the radius of curvature of actual space.

With this identification the term elementary "wave systems" proves to be a misnomer. The apparent change of ψ represents merely the difference between the covariant derivative and the ordinary derivative in spherical co-ordinates. In a physical sense ψ represents uniform distribution round a great circle, and the periodicity in its analytical expression corresponds to the periodicity of the circle. The mass and momentum associated with ψ has a purely geometrical origin, depending on the fact that the momentum operator $\partial/\partial x_\mu$ does not vanish although the covariant derivative of ψ vanishes.

Consider the alternative, viz., that ρ is not to be identified with the radius of actual space although it is of the same order of magnitude. Then in addition to the effect of curvature we must have an absolute wave in ψ. That would mean that the mass of S_2 comes from two sources, the one an effect of world curvature and the other an arbitrary periodicity of which we can say no more than that it is innate in the primitive constituents of the universe. That is æsthetically unattractive. But the decisive objection is that S_2 is the meeting point of the macroscopic and microscopic parts of the theory and its mass therefore appears in both theories. In macroscopic (relativity) theory mass is a purely geometrical consequence of the curvature of space-time ; the *same mass* cannot change its character when it passes into microscopic theory and become partly a geometrical consequence of the curvature and partly something else. Clearly the only consistent theory must exhibit the mass of the electron as a purely geometrical consequence of space-time curvature just as the mass of the gram standard is already known to be.

It may be added that, whereas in quantum theory mass is the component of a vector p^α, in relativity theory it is the component of a tensor $T^{\alpha\beta}$ which for a simple system would be the square $p^\alpha p^\beta$ of the vector p^α. Thus the first theory connects mass with the curvature of a great circle $1/\rho$ and the second with the Gaussian or spherical curvature $1/\rho^2$. Owing to this difference of dimensions the connection of microscopic and macroscopic units has to be made under standardized conditions, viz., in uniform space of radius equal to that occurring in our actual universe.

The radius ρ is the "de Sitter radius" connected with the cosmical constant λ by the equation

$$\lambda = 3/\rho^2. \qquad (9.4)$$

This is not immediately obvious, because we have defined ρ (like R_1, R_2) by reference to stereographic co-ordinates and these have not generally been employed in relativity theory. But we can show directly that the line element (4.1) extended to the four co-ordinates of space-time satisfies

$$G_{\mu\nu} = (3/R^2)g_{\mu\nu},$$

so that the corresponding cosmical constant is identified. From (6.6) and (9.3) we have

$$m_2 = \frac{h}{4\pi c}\frac{\sqrt{N}}{\rho}, \tag{9.5}$$

so that (8.5) now determines the mass of an electron or proton in terms of $\sqrt{N}/\rho$, a quantity which has been tentatively evaluated from observations of the recession of spiral nebulæ. But the result (9.5) probably requires a correcting factor discussed in § 11.

10. It may be asked: Do you suggest that 10^{79} particles, mostly in remote parts of the universe are in some way responsible for the effects we observe when we perform experiments to determine the mass of an electron? Certainly not. The system of 10^{79} particles is an intermediary comparison system which is eliminated when the mass of the electron is expressed in terms of the gram. Any other intermediary must lead to the same result, but the theory is much more difficult.

The position is this. If microscopic (quantum) theory and macroscopic (relativity) theory are kept entirely separate, all microscopic masses will be expressed in terms of some particular microscopic unit μ_1, and all macroscopic masses in terms of a macroscopic unit μ_2. To compare the electron with the gram we must find the ratio μ_1/μ_2. This requires that we consider some object (actual or ideal) and work out theoretically its dynamical behaviour, (*a*) as a collection of particles governed by microscopic theory, and (*b*) as an integral body governed by macroscopic theory, so as to be able to state its mass in both systems of units. Any object will serve, provided the theory is far enough developed to treat it. I use the universe because that is the only object I feel able to treat.

The difficulty in using an ordinary solid for this purpose is to deal with the field of force which keeps the particles together instead of letting them stray over the universe. Unless we have a complete theory of this force we cannot proceed. In statistical mechanics we often discuss glibly n particles moving inside a spherical vessel of radius r. Suppose that we use this ideal system as an intermediary. At or near the boundary we must place a field of inward acceleration so intense that no particle has any probability of passing the boundary. (A minute probability of exit would empty the vessel, for there is next to no probability of a particle re-entering.) By Einstein's theory this field of acceleration involves a strong curvature of space-time. Either we must embark on the theory of statistics in space of variable metric; or we must adopt a field of acceleration corresponding to uniform metric of such curvature that no particle can pass beyond a distance r however great its velocity. In the latter case the interior of the vessel becomes a hemisphere of spherical space. Thus the problem again reduces to the study of a closed spherical "universe." Incidentally we must make sure that the electron and the gram weight are inside this new universe before we allow the spherical space to close up. So with the new intermediary, we shall find what *would be* the ratio of the mass of an electron to that of a gram weight in a space whose curvature is enormously greater than that of our actual universe—a matter of no practical interest.

11. A rather difficult point arises in connecting the phase space of an electron with ordinary space. The electron has a spin co-ordinate which takes four discrete values, so that it may be said to require ordinary space represented four times over. Again a unit cell of phase space (as ordinarily calculated) can contain two electrons of opposite spin and presumably also two protons—as though it were formed by coalescence of four original cells.

We have represented the strain vector at the origin by an algebraic number. But an algebraic number is not a *pure* wave tensor, *i.e.*, it is not the product of two vectors. I have examined the conditions of factorization elsewhere.† A non-degenerate pure wave tensor is of the form

$$\tfrac{1}{4}(\pm E_{12} \pm E_{34} \pm E_{50} + E_{16})k, \tag{11.1}$$

in which the four E-symbols are such that they mutually commute. To obtain an algebraic wave tensor $E_{16}k$, we must add four pure wave tensors suitably varying the signs in (11.1). It is fairly evident that the four constituents represent charges of opposite sign and charges of opposite spin.

Thus from several different points of view our space appears as a coalescence of four partial spaces.

This point arises when we attempt to factorize $\psi_\alpha \phi_\gamma \chi_\beta \omega_\beta$. Since $\chi_\beta \omega_\beta$ is algebraic (of the form $E_{16}k$) it cannot be factorized, and I have accordingly written → instead of = in (8.1); but it is the sum of 4 factorizable quantities of the form (11.1). Physically it is the resultant of N factorizable quantities

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† 'J. Lond. Math. Soc.,' vol. 8, p. 142 (1933).

$\chi'\omega'$ contributed by the N particles of the universe. For independent particles the resultant is formed by the $\sqrt{N}$ law as shown in § 9. We have now to notice that $\chi_\beta\omega_\beta$ is the random resultant of N/4 algebraic constituents; but the further dissection of each of these constituents into 4 particles with separable wave vectors χ', ω' is not a random process, but is the analytical resolution of an algebraic quantity into factorizable constituents. The four constituents have a definite mathematical relation to one another such that when one is fixed the others are determined; their algebraic components are simply additive. This substitution of the additive law for the $\sqrt{N}$ law increases the resultant in the ratio 4 to $\sqrt{4}$, so that our former value has to be multiplied by 2.

The physical interpretation is that the macroscopic standard (*e.g.*, the gram weight) is supposed to be electrically neutral *by nature.* We cannot trust to the charges balancing out by the law of average. Consideration of numerical values at once shows there is no such balance. If it is an even chance that each of the 10^{79} particles of the universe is positive or negative, we may expect an excess of $10^{39\cdot5}$ particles of one sign. This is enough to make the electrostatic force in the universe comparable with the gravitational force. We have therefore to provide specifically for the balancing of charge, and similarly of spin.

Inserting this factor 2 in (9.5) we have

$$m_2 = \frac{h}{2\pi c}\frac{\sqrt{N}}{\rho}. \tag{11.2}$$

The value of $\sqrt{N}/\rho$ found from (11.2) and (8.5) gives a limiting speed of recession of the spiral nebulæ 778 km. per second per megaparsec. It also gives $N = 1\cdot75 . 10^{79}$. These figures are provisional since the relation between $\sqrt{N}/\rho$ and the recession of the nebulæ ought to be reinvestigated from the new point of view; but that is not within the scope of the present paper.

12. The principle of the foregoing determination of the masses of the electron and proton can perhaps be most easily understood from the point of view of wave packets. The connection between wave mechanics and classical mechanics is contained in the fact that a small wave packet behaves approximately as a classical particle. The classical behaviour, however, gives no indication of the scale of the wave structure; this can only be found by studying phenomena in which the wave packet differs from a particle, viz., diffraction effects. A wave packet disperses at a rate depending on the square of the proper mass according to a formula worked out by Darwin. In wave mechanics $(\text{mass})^2$ is most

appropriately defined as a coefficient determining the rate of spread of a wave packet; the square root is an abstraction, and the positive sign attributed to it is conventional.

These wave packets are created by our observations, or rather by our *knowledge* of the results of observation. When a measurement is made, a probability distribution becomes condensed into a narrow range. The wave packets have no pre-history and occur as discontinuities in the mathematical representation of the universe. After their creation they disperse. The fact that the wave packets arise discontinuously and spread towards the future appears to be the source of the one-way texture of time in physics.

Anything that is supposed to have been observed must correspond to a dispersing wave packet. For example, we say that an object is located at (x, y, z); if the location signifies something observable, (x, y, z) must be a dispersing wave packet not a geometrical point. (This is in addition to the wave packet corresponding to the object itself.) For (x, y, z) has to be identified with reference to some material system and in making the measurements indicated, we give an unknown kick to the material system; consequently a point defined with reference to it becomes more and more uncertain as time elapses. In current physics we have assumed that observable locations correspond to geometrical points and have thrown the whole "uncertainty" on to the object observed in that location. It is this substitution which we are examining in the present investigation.

We can only observe relations. Therefore if we attribute a wave system to a single entity, *e.g.*, an electron, we can never create a wave packet directly in that system. Observation and measurement can only create a wave packet in a double wave system; the subsequent dispersal is that of a double wave packet. The simple wave packets treated in current theory are obtained by analytical resolution of the wave packets created in double wave systems; they are then regarded as having an independent existence and a mass is assigned as a coefficient determining the rate of dispersal. But it is clear that a stringent relation between the rates of dispersal of the double wave packet and of the two single wave packets must be satisfied if the latter continue to be equivalent to the former. This condition is the basis of our equation (8.5).

In practice if we measure the position of an electron we refer it to some very massive object of reference, *e.g.*, the earth; we thus create a wave packet in the earth-electron wave function. A little later this wave packet has spread out considerably, and we may make another measurement to reconcentrate the probability. At first sight it seems pedantic to insist that the wave which we reconcentrate is the double earth-electron wave, not the simple electron wave; for the position of the earth has not become appreciably uncertain in the short interval. The wave-lengths being inversely proportional to the masses, the earth wave is of order 10^{-50} of the electron wave. Whether the approximation $10^{-50} = 0$ is legitimate, depends on what we are trying to determine by the measurements. Suppose that they are part of a series of experiments to determine the mass of the electron. In order not to complicate matters by introducing more objects than necessary let us use the earth as the standard of mass; the mass of the electron is then of order 10^{-50}. Evidently the approximation $10^{-50} = 0$ would stultify the experiment.

In an observational determination of the mass of the electron there are two indispensibles, viz., the electron and the standard mass employed; and, directly or indirectly, our observations relate to a double wave function of these. However great the disparity of mass this must not be treated as a single wave function; for that is equivalent to treating the mass of the standard as infinite—which makes it useless as a standard.

The origin of the mass m_2 of our comparison system S_2 can be understood by reference to the Uncertainty Principle. If we know nothing about a particle except that it is in spherical space of radius ρ, we may describe its uncertainty of position as ρA, where A is a unit vector in an uncertain direction in the space in which the sphere is represented. The corresponding uncertainty of momentum is $(h/2\pi\rho) A'$, *i.e.*, a definite momentum $h/2\pi\rho$ in an uncertain direction A′. The mean of N such particles has an uncertainty of position $(\rho/\sqrt{N}) A$, and correspondingly a momentum $h\sqrt{N}/2\pi\rho$ in an uncertain direction. Dividing by c we obtain the proper mass $m_2 = h\sqrt{N}/2\pi\rho c$ found in (11.2).

It may be noticed that, in the present theory, space, which has the radius of curvature ρ, is not empty in the strict sense, *i.e.*, *known* to be empty, but space in which the particles have their *a priori* probability distribution both as regards density and momentum. This is a change of view, because the equation $G_{\mu\nu} = \lambda g_{\mu\nu}$ is generally supposed to refer to strictly empty space; but I think it improves the theory in every way. *A priori* probability distribution of energy and momentum now determines the curvature which in turn determines the metric. Thus *a priori* probability and metric are represented by tensors whose transformations correspond, and the equations of physics become invariant for all changes of the assumed *a priori* probability. This is as it should be, for *a priori* probability is obviously not an observable.

The question may be raised whether in intergalactic regions, where the density is definitely below the average for the whole universe, the curvature is smaller than the " natural curvature " given by the cosmical constant which has hitherto been regarded as the minimum. Our equations will exhibit it as smaller, but I doubt if this expresses anything that could be observed. There must be a lower limit to the curvature detectable observationally by triangulation. Measurements cannot be carried round a triangle in less time than light takes to travel, so that the position of the first vertex has become uncertain by the time we reach it again. We can reduce uncertainties by bringing in a large number of particles as reference points ; but if there is a *large* number of particles in the region the corresponding curvature will be large. I think, therefore, that when our equations assert that a reduction of the number of particles below the average diminishes the curvature below the natural curvature, the reduction will of itself prevent our testing the statement observationally.

13. The employment of strain vectors in this investigation requires some further explanation. In current wave mechanics the wave functions ψ, ϕ are taken to be conjugate complex quantities. To preserve conjugacy their transformations must be of the form

$$\psi \to e^{a+ib}\,\psi, \qquad \phi \to e^{a-ib}\,\phi,$$

so that the real and imaginary parts of the transformation become separated. Our strain vectors are the matrix generalization of these conjugate products their space-like and time-like transformations being separated in the same way as the above real and imaginary transformations of $\psi\phi$. (*Cf.* (2.4) and (2.5).)

The conception of a " combined system " presupposes that we have laid down (arbitrarily) a reckoning of simultaneity for the two parts and therefore a separation of space and time. Otherwise the times associated with the separate parts cannot be replaced by a single time for the whole system. Lorentz transformations do not apply to the combined system† ; to change the reckoning of simultaneity we should have to separate the two parts, apply the Lorentz transformation to each, and then recombine them. Space vectors, which owe their importance to Lorentz invariance, are therefore not required. The observables are associated with changes of the internal state of the combined system ; these are clearly of the nature of strains and describable by strain vectors.

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† There is no more reason for using Lorentz-invariant equations for the internal constitution of the atom than for the internal constitution of the stars.

Whilst strain vectors appear naturally in the description of a combined system, it seems odd to contemplate strain vectors attached to a single particle. What is being strained ? The answer is that the strain vector has not been attached to the particle, but the particle is an abstract conception that has been attached to a strain vector which we have obtained by a mathematical factorization. No question of observability arises until the particle is combined with some other system and we return to double strain vectors.

We can, however, make a one-to-one correspondence of simple strain vectors with space vectors in the following way. This correspondence associates a space vector with the particle and gives us a more picturable conception of it, viz., as having position and momentum. Consider the five-dimensional continuum corresponding to a pentad E_1, E_2, E_3, E_4, E_5, the real matrices being E_4, E_5. We shall denote by e_μ the covariant wave tensor (or strain vector) which has the value E_μ in the co-ordinate system initially chosen. The strain vector e_{45} has the important property that it is invariant for all 10 rotations of the axes in five dimensions. This is easily verified, remembering that by (2.4) and (2.5) a strain vector is unaltered by transformations corresponding to real matrices with which it commutes and to imaginary matrices with which it anticommutes. No other strain vector has this invariant property.† Thus for all orientations of axes $(e_{45})_{\alpha\beta} = E_{45}$.

If a covariant wave vector ϕ and a contravariant wave vector χ are associated by the relation

$$\phi_\beta = \chi^\alpha a_{\alpha\beta},$$

$a_{\alpha\beta}$ must be a covariant wave tensor and therefore a strain vector. Consider the particular association given by $a_{\alpha\beta} = (e_{45})_{\alpha\beta}$; then

$$\phi = \chi^* E_{45}, \tag{13.1}$$

and this relation persists unchanged however the axes in five dimensions are rotated. (The asterisk is used to distinguish an initial vector when suffixes are omitted.)

Now E_{45} is a real four-point matrix, *e.g.*,

$$\begin{matrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{matrix}$$

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† It may be compared with the mixed tensor δ_μ^ν and the contravariant vector density $\epsilon_{\alpha\beta\gamma\delta}$ which likewise have fixed numerical values.

This would give

$$\chi_1, \chi_2, \chi_3, \chi_4 = \phi_2, -\phi_1, -\phi_4, \phi_3. \qquad (13.2)$$

Thus the covariant vector is turned into an associated contravariant vector by renumbering the components and changing signs.† This may be regarded as a definition of "raising the suffix" in wave-tensor calculus.

A sum or integral $\Sigma\psi\phi dv$ in strain vector representation becomes $\Sigma\psi\chi^* \mathrm{E}_{45} dv$ in space vector representation. By the elementary properties of the E_μ, $\mathrm{E}_{45} = i\mathrm{E}_1\mathrm{E}_2\mathrm{E}_3$; so that the element $\mathrm{E}_{45}dv$ which multiplies the space vector $\psi\chi^*$ is expressible as a product $\mathrm{E}_1 dx_1 \mathrm{E}_2 dx_2 \mathrm{E}_3 dx_3$. Since E_1, E_2, E_3 give the three space-like directions, the element of integration appears as a volume element of three dimensional space. In strain vector representation the element is an algebraic weight factor dv without directional characteristics.

Let

$$\psi\chi^* = \mathrm{J} = \Sigma \mathrm{E}_\mu j_\mu, \qquad \psi\phi = \mathrm{K} = \Sigma \mathrm{E}_\mu k_\mu. \qquad (13.3)$$

The components $j_{15}, j_{25}, j_{35}, j_{45}$ constitute the momentum vector. Here the time direction is taken to be E_4, so that E_5 is normal to space-time and E_{45} corresponds to the rotation which would carry a point forward in the time direction. From (13.2) and (13.3) we find

$$\Sigma \mathrm{E}_\mu k_\mu = \Sigma \mathrm{E}_\mu \mathrm{E}_{45} j_\mu. \qquad (13.4)$$

In particular $j_{45} = -ik_{16}$. Thus the component associated with time displacement in space-vector representation becomes the algebraic component in strain vector representation.

This double aspect of time is one which I have dealt with from a different standpoint in earlier papers.‡ In Dirac's theory time t is an internal coordinate in the "state" of a system which extends from $t = -\infty$ to $t = +\infty$. But inasmuch as the state is supposed to be capable of change, there is also a proper time s external to the state to which these changes of state are correlated. This is invariant for all relativistic transformations of the state and must therefore correspond to the invariant matrix E_{16}. When strain vectors are introduced, the reckoning of simultaneity becomes fixed and there is a unique correspondence of t and s; the units are naturally chosen so that they agree.

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† We lose the six transformations which are not rotations of five dimensional space and for which e_{45} is not invariant. But the importance of space vectors is that they represent the ordinary vectors (and 6-vectors) of physics, so that there is no harm in prohibiting transformations which are never applied to the ordinary vectors of physics.

‡ 'Proc. Roy. Soc.,' A, vol. 133, p. 322 (1931).

Any displacement of s will be common to all three systems S_1, S_2, S_{12}, since the purpose of s is to provide an extraneous variable to which their changes of state are correlated. It is for this reason that X^2 is taken to be the same for the three systems in (8.3).

By (13.4) each component j_μ is equal to a component k_ν (sometimes with a factor i). We find that the 10 components of k_μ in phase space correspond to the components of j_μ in the directions of the 10 rotations of space-time. In other words, the space vector representation of the particle pictures the strain as being produced by translation or spin of the particle. Since, however, we work with strain vectors we have described the character of the displacement by the character of the strain produced and not by the character of the motion attributed to the particle.

The γ-Rays of Radium (B + C) *and of Thorium* (C + C′).

By C. D. Ellis, F.R.S.

(Received October 2, 1933.)

Reliable information about the γ-rays emitted by radium C′ is particularly valuable since the main features of the nuclear level system are shown by the groups of long range α-particles and are hence accessible to direct investigation. These long range groups of α-particles have been measured recently by Rutherford, Lewis and Bowden* by a greatly improved method which has not only brought to light several new groups, but in addition has given considerably greater accuracy in the determination of the energies of the groups than had been possible in the past. The energy of these groups in excess of that of the normal group is a measure of the excitation energy of the nucleus and the older measurements had indicated, as was to be expected, a close correspondence between these energies and the quantum energies of the γ-rays. The recent more accurate measurements of Rutherford, Lewis and Bowden provided the opportunity of a more rigorous test of this connection and showed the possibility, by the combination of the information from these two sources, of a direct experimental determination of the level system. However, the accuracy of the published data on the Ra C γ-rays deduced from the natural

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* 'Proc. Roy. Soc.,' A, vol. 142, p. 347 (1933).

β-ray spectrum was subject to some doubts for the following reasons. The measurements dated from 1924 when the absolute energies of certain strong groups in the β-ray spectrum were measured* and the energies of the remaining lines determined by relative measurements. The strong groups in question lay between $0 \cdot 4 \times 10^5$ and $3 \cdot 0 \times 10^5$ volts and the procedure of step-wise comparison up to energies of over 2×10^6 volts may have led to cumulative errors. More serious was that recent measurements† on the Th (B + C) β-ray spectrum had thrown doubt on the correctness of the absolute values. Lastly, experiment gives values for $H\rho$, that is the momenta of the electrons in the groups, and the calculation of the energies involves *e*/*m*. The older data had been based on $e/m = 1 \cdot 769 \times 10^7$, and while the change to the value $1 \cdot 760 \times 10^7$ alters the energies proportionally far less, there was involved here an avoidable error which had to be removed.

These considerations justified fresh experiments on these much measured spectra. Although the experiments were lengthy and laborious it is not necessary to enter into a detailed description, since the apparatus and methods were the same as that used in the investigation of the β-ray spectrum of Th (B + C) (Ellis, *loc. cit.*). It will suffice to say that independent absolute determinations were made throughout the whole spectrum, and that all the energies were recalculated using $C = 2 \cdot 9980 \times 10^{10}$ and $e/m = 1 \cdot 760 \times 10^7$. Some of the fainter groups from Ra C require long exposures and rather special conditions to render them measurable, and where suitable measurements could not be made the $H\rho$ values were interpolated, using the older experiments. This procedure was justified since the former relative values of $H\rho$ were confirmed to one part in a thousand even over wide ranges. The main difference is that the new values are all about one part in two hundred lower, as was to be expected from the results with Th (B + C). I estimate that the limits of error in the energies are about one part in five hundred, and about one part in two thousand in the relative values.

The detailed comparison of these results with the α-ray measurements has been given by Rutherford, Lewis and Bowden, but it is important to note that the excellent agreement is evidence of the substantial accuracy of both measurements, since they are entirely independent, and even different standardizing apparatus was used.

It is convenient to include in this paper certain measurements on the Th (C + C′) spectrum which it was impossible to make at the time of the previous investigation. They are interesting since they agree excellently with and extend the information obtained from the α-rays.

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* Ellis and Skinner, 'Proc. Roy. Soc.,' A, vol. 105, pp. 165, 185 (1924).

† Ellis, 'Proc. Roy. Soc.,' A, vol. 138, p. 318 (1932).

The γ-rays of Ra B . C and Ra C . C′.

It is hoped that the tables which follow are self-explanatory. A name is assigned to each β-ray line for convenience in referring to it. This assignment is quite arbitrary and has no special significance; the general principle underlying the system of nomenclature was discussed in a letter to 'Nature.'* The intensities given are those determined by Ellis and Aston. Throughout the tables more figures are given in the entries than are justified by the estimated accuracy since this facilitates checking the calculations. A few new lines have been found and are listed provisionally under Ra B; their real origin is not known.

β-ray Spectrum of Ra B.

(+ signifies lines not included in the analysis.)

Name.	Old Hρ.	New Hρ.	New log Hρ.	Intensity electrons per disintegration × 10^4.		Energy volts × 10^6.
A	660·9	657·66	81800	240	Visual estimation.	0·3674
Aa	670·0	663·45	82181	40		0·3737
Aa1	687·0	683·99	83505	8		0·3963
Aa3	—	725·47+	86062	20		0·4439
Aa4	—	746·78+	87319	8		0·4692
B	768·8	762·66	88233	80		0·4885
Ba	—	764·66	88347	24		0·4910
Ba1	—	769·25	88607	4		0·4966
C	793·1	787·25	89611	40		0·5190
Ca	799·1	798·13	89934	10		0·5204
Cg	—	890·8+	—	6		0·6562
Cj	—	983·85+	—	3		0·7906
D	1155	1146·9+	05953	11		1·0497
Da	1209	1200·6+	07939	5		1·1412
F	1410	1400·4	14625	425		1·5044
Fa	1496	1485·9+	17200	21		1·6699
Fb	1576	1565·5+	19465	11		1·8292
G	1677	1665·9	22165	480		2·0364
Ga	1774	1762·4	24610	53		2·2415
Ga1	1832	1820·1	26010	13		2·3668
Ga3	1850	1838·0	26435	3		2·4061
H	1938	1925·5	28455	530		2·6004
Ha	2015	2002·2	30150	64		2·7741
Ha1	2064	2050·9	31194	11		2·8837
Ha3	2110	2096·6+	32152	8		2·9919
I	2256	2241·9	35061	85		3·3343
Ia	2307	2292·6	36033	42		3·4558
Ia1	2321	2306·6	36297	8		3·4895
Ia3	2433	2418·0+	38345	8		3·7607
Ia4	2480	2464·7+	39177	8		3·8754

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* Ellis, 'Nature,' vol. 129, p. 276 (1932).

Analysis of Ra B β-ray Spectrum.

β-ray line.		Intensity electrons per disintegration $\times 10^4$.		Level of conversion.	Energy volts $\times 10^{-5}$.	Absorption energy volts $\times 10^{-5}$.	$h\nu$ of γ-ray volts $\times 10^{-5}$.
γA	A	240	Visual estimation.	L_I	0·3674	0·1634	0·5308
	Aa	40		L_{II}	0·3737	0·1567	0·5304
	Aa1	8		L_{III}	0·3963	0·1338	0·5301
	B	80		M_I	0·4885	0·0399	0·5284
	Ba	24		M_{II}	0·4910	0·0368	0·5278
	Ba1	4		M_{III}	0·4966	0·0317	0·5283
	C	40		N_I	0·5190	0·0093	0·5283
	Ca	10		O	0·5264	0·0020	0·5284
						Mean 0·529 × 10^5 volts.	
γF	F	425		K	1·5044	0·9030	2·4074
	Ga	53		L_I	2·2415	0·1634	2·4049
	Ga1	13		M_I	2·3668	0·0399	2·4067
						Mean 2·406 × 10^5 volts.	
γFa	Fa	21		K	1·6699	0·9030	2·5729
	Ga3	3		L_I	2·4061	0·1634	2·5695
						Mean 2·571 × 10^5 volts.	
γG	G	480		K	2·0364	0·9030	2·9374
	Ha	64		L_I	2·7741	0·1634	2·9375
						Mean 2·937 × 10^5 volts.	
γH	H	530		K	2·6004	0·9030	3·5034
	I	85		L_I	3·3343	0·1634	3·4977
	Ia	42		M_I	3·4558	0·0399	3·4957
	Ia1	8		N_I	3·4895	0·0093	3·4988
						Mean 3·499 × 10^5 volts.	

β-ray Spectrum of Ra C.

Name.	Old Hρ.	New Hρ.	New log Hρ corrected.	Intensity electrons per disintegration $\times 10^4$.	Energy volts $\times 10^{-5}$.
Aa2	703	698·7	84430	(2) visual	0·4130
Da1	1379	1369·6	13658	0·5	1·4462
F1	1438	1428·3	15481	0·5	1·5578
Fa1	1557	1546·6	18938	5·3	1·7910
Fb1	1594	1583·4	19959	1·0	1·8657
Ga2	1834	1822·1	26057	1·0	2·3712
Ga4	1912	1899·7	27868	0·5	2·5427
Ha2	2085	2071·8	31634	2·6	2·9343
Ha4	2156	2142·4	33090	0·5	3·0988
I1	2256	2241·9	35061	1·6	3·3343
Ia2	2390	2375·2	37570	0·5	3·6560
Nb	2550	2534·4	40387	0·5	4·0482
Nc	2720	2703·6	43194	1·0	4·4735
Nc1	2840	2823·0	45071	0·5	4·7777
Nc2	2890	2872·8	45830	0·5	4·9061

β-ray Spectrum of Ra C—(continued).

Name.	Old Hρ.	New Hρ.	New log Hρ corrected.	Intensity electrons per disintegration $\times 10^4$.	Energy volts $\times 10^{-5}$.
O	2980	2962·3	47163	40	5·1377
O1	3145	3126·5	49506	2·6	5·5672
O2	3203	3184·3	50301	2·6	5·7203
P	3271	3251·9	51214	9·0	5·8989
P1	3307	3287·8	51690	1·6	5·9945
P2	3326	3306·7	51939	1·6	6·0451
Pa	3584	3563·4	55187	3·2	6·7344
Pa1	3824	3802·3	58005	2·1	7·3842
Q	4196	4172·7	62042	4·1	8·4084
Qa	4404	4379·9	64146	2·6	8·9821
R	4866	4839·7	68482	13	10·275
R1	4991	4964·3	69586	1·0	10·628
Ra	5136	5108·7	70831	2·1	11·040
Ra1	5178	5150·5	71185	1·0	11·157
S	5281	5253·0	72041	3·6	11·449
S1	5428	5399·3	73234	0·85	11·866
Sa	5552	5522·9	74217	0·85	12·221
Sa1	5615	5585·6	74707	0·2	12·400
Sb	5775	5744·9	75928	0·9	12·859
T	5904	5873·3	76888	25	13·228
T1	5948	5917·0	77210	1·0	13·355
T2	6030	5998·2	77802	0·4	13·588
U	6161	6127·9	78731	3·7	13·962
Ua	6212	6178·0	79085	1·4	14·107
Ua1	6322	6286·5	79841	0·2	14·421
Ua2	6385	6348·3	80266	0·2	14·601
Ua3	6480	6441·8	80901	0·4	14·869
Ua4	6523	6484·4	81187	0·25	14·992
Ua5	6656	6615·3	82055	0·25	15·372
Ua6	6735	6603·3	82564	0·2	15·598
Ua7	6800	6757·4	82978	0·25	15·784
Ua8	6932	6887·8	83808	0·2	16·165
Ub	6998	6952·8	84216	0·7	16·355
V	7109	7062·7	84897	4·2	16·671
Va	7154	7106·9	85168	0·85	16·806
Va1	7240	7192·0	85685	0·30	17·053
Vb	7380	7330·8	86515	0·95	17·456
Vb1	7530	7479·3	87386	0·2	17·890
Vb2	7690	7637·5	88295	0·2	18·354
Vb3	7823	7768·7	89035	0·2	18·737
Vc	7974	7918·3	89863	0·4	19·175
Vc1	8090	8033·0	90488	0·2	19·512
Vd	8313	8253·7	91665	0·4	20·160
Ve	8457	8396·0	92407	0·4	20·578
W	8617	8554·2	93218	0·95	21·043
Wa	8674	8610·5	93503	0·4	21·208
Wa1	8885	8819·2	94543	0·2	21·822
Wa2	9068	8999·9	95424	0·2	22·354
Wa3	9165	9095·8	95884	0·2	22·637
Wa4	9425	9352·5	97093	0·2	23·393
Wa5	9655	9580·1	98137	0·2	24·067
Wa6	10020	9941·0	99743	0·2	25·132

Analysis of Ra C β-ray Spectrum.

β-ray line.		Intensity electrons per disintegration $\times 10^4$.	Level of conversion.	Energy volts $\times 10^{-5}$.	Absorption energy volts $\times 10^{-5}$.	$h\nu$ of γ-ray volts $\times 10^{-5}$.
γO	O	40	K	5·1377	0·9301	6·0678
	P	9·0	L_I	5·8989	0·1687	6·0676
	P1	1·6	M_I	5·9945	0·0413	6·0358
	P2	1·6	N	6·0451	0·0098	6·0549
					Mean 6·067 × 10^5 volts.	
γPa	Pa	3·2	K	6·7344	0·9301	7·6645
					7·66 × 10^5 volts.	
γQ	Q	4·1	K	8·4048	0·9301	9·3349
					9·33 × 10^5 volts.	
γR	R	12·8	K	10·275	0·930	11·205
	Ra	2·1	L_I	11·040	0·169	11·209
	Ra1	1·0	M_I	11·157	0·041	11·198
					Mean 11·20 × 10^5 volts.	
γS	S	3·6	K	11·449	0·930	12·379
	Sa	0·85	L_I	12·221	0·169	12·390
					Mean 12·38 × 10^5 volts.	
γSb	Sb	0·9	K	12·859	0·930	13·789
					13·79 × 10^5 volts.	
γT	T	25·2	K	13·228	0·930	14·158
	U	3·7	L_I	13·962	0·169	14·131
	Ua	1·4	M_I	14·107	0·041	14·148
					Mean 14·14 × 10^5 volts.	
γV	V	4·2	K	16·671	0·930	17·601
	Vb	0·95	L_I	17·456	0·169	17·625
					Mean 17·61 × 10^5 volts.	
γW	W	0·95	K	21·043	0·930	21·973
	Wa1	0·2	L_I	21·822	0·169	21·991
					Mean 21·93 × 10^5 volts.	

Note.—Two other γ-rays γI1 4·26 and γNb 4·98 may be added from evidence from the excited spectrum. The remaining β-ray lines must be taken as weak K lines.

In a provisional nomenclature adopted before the analysis was complete γI_1 was named γNa and γSb was named γSa. Reference is made to this since these latter names are inserted in Fig. 3 of a paper by Rutherford, Lewis and Bowden, 'Proc. Roy. Soc.' A, Vol. 142, p. 347 (1933). No confusion will arise, however, since the energies used are those given above.

Some Additional Data on the β-ray Spectra of Th (C + C′ + C″).

In the previous investigation* of these bodies an important group of low energy lines was not measured. The following table replaces therefore that section of Table II on p. 325* labelled "Not Measured."

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* Ellis, 'Proc. Roy. Soc.,' A, vol. 138, p. 318 (1932).

Name.	Log Hρ.	Hρ.	Energy volts × 10^{-5}.	Visual intensity.
A	72957	536·50	0·2473	100
Aa	73435	538·95	0·2527	10
Ab	75169	564·53	0·2731	2
B	81463	652·57	0·3619	40
Ba	81654	655·45	0·3650	1
Bb	83144	678·33	0·3901	15
Bc	83568	685·00	0·3975	3

These lines are due to the γ-ray of $0{\cdot}399 \times 10^5$ volts, as is shown by the following analysis, and as is generally accepted this corresponds to the difference in energy of two of the α-ray groups emitted by Th C . C″.

Origin.	Energy of β-ray line absorption energy in volts × 10^{-5}.
L_I	$0{\cdot}2473 + 0{\cdot}1530 = 0{\cdot}4003$
L_{II}	$0{\cdot}2527 + 0{\cdot}1466 = 0{\cdot}3993$
L_{III}	$0{\cdot}2731 + 0{\cdot}1262 = 0{\cdot}3993$
M_I	$0{\cdot}3619 + 0{\cdot}0369 = 0{\cdot}3988$
M_{II}	$0{\cdot}3650 + 0{\cdot}0340 = 0{\cdot}3990$
N_I	$0{\cdot}3901 + 0{\cdot}0084 = 0{\cdot}3985$
O	$0{\cdot}3975 + 0{\cdot}0010 = 0{\cdot}3985$
	Mean .... $0{\cdot}399 \times 10^5$ volts γA.

In addition the following line has been found in this region; its origin is unknown.

Name.	Log ρ.	Hρ.	Energy volts × 10^{-5}.	Visual intensity.
A1	73155	538·95	0·2495	1

The γ-rays corresponding to the Long Range α-rays of Th C . C′.

From observations of the long range α-particles emitted by Th C it appears that the Th C′ nucleus can be left with either $7{\cdot}26 \times 10^5$ volts or $17{\cdot}97 \times 10^5$ volts excitation energy. A β-ray group corresponding to the smaller excitation had already been detected* and a careful search was made for that line corresponding to the higher excitation. The following two lines were found:—

Hρ.	Energy volts × 10^{-5}.	Intensity electrons per disintegration × 10^4.
6591	15·30	1·2
7207	17·09	0·5

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* Ellis, *loc. cit.*, p. 387.

The intensities are calculated on the assumption that these lines come from Th C . C′. They suggest γ-rays of $16 \cdot 23 \times 10^5$ volts and $18 \cdot 02 \times 10^5$ volts. The second of these agrees with the evidence from the long range α-particles. It is interesting to calculate the intensities of these γ-rays on the alternative assumption that these are dipole or quadripole transitions. The calculated values are taken from Hulme* and from Taylor and Mott.†

γ-ray volts $\times 10^{-5}$.	Electrons per disintegration $\times 10^{-5}$.	Calculated internal conversion $\times 10^8$.		Quanta per disintegration.	
		Dipole.	Quadripole.	Dipole.	Quadripole.
7·26	75	3·9	11·9	0·2	0·06
18·02	5	0·8	2·3	0·06	0·02

The well-known difficulty in detecting any γ-radiation from Th C′ suggests that at least the first γ-ray is probably due to a quadripole transition.

Summary.

Information about the nuclear level system of certain radioactive bodies can be obtained both from the long range α-particles emitted and from the γ-ray spectra. Particular importance attaches to the comparison of these two methods. Great improvements have been effected recently in the measurement of the energy of the long range α's, and it became necessary to improve also the accuracy of the γ-ray determination. The present communication describes a remeasurement of the Ra (B + C) spectrum and certain other measurements on the Th (C + C′) spectrum which were necessary to complete investigations already published.

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* ‘Proc. Roy. Soc.,’ A, vol. 138, p. 643 (1932).

† ‘Proc. Roy. Soc.,’ A, vol. 138, p. 665 (1932).

Anomalous Dispersion and Absorption of X-Rays.

By E. J. Williams, Manchester University.

(Communicated by W. L. Bragg, F.R.S.—Received July 29, 1933.)

The general nature of the anomalous dispersion of X-rays, and its relation to absorption, was considered by Kallmann and Mark in 1927.* The purpose of this paper is first to make more detailed calculations of the dispersion for certain special cases; secondly, to consider the theoretical reasons for the observed value of the oscillator strength, particularly the equivalence of the 2K electrons to about 1·3 classical electrons.†

By virtue of the general applicability of the electromagnetic theory of radiation an atom in quantum mechanics is in many respects equivalent to a multitude of classical oscillators. The dispersion and absorption of radiation by the atom depend upon the frequency and strength of these virtual oscillators. In calculating the dispersion of X-rays there are two courses open. We can either use approximate estimates of the theoretical quantum-mechanical strength of the oscillators concerned, or use the theoretical relation which exists between the oscillator strength and the intensity of absorption of radiation, and assume the experimental values of the latter. The second procedure is possible since the necessary experimental data are available, and we adopt this procedure here because the accuracy of this data is greater than the accuracy with which the theoretical oscillator strength can be evaluated. Kallmann and Mark, in their treatment of dispersion, also adopt the same procedure so far as they assume that the variation of the oscillator strength with frequency corresponds to the λ^3-law of photoelectric absorption. The dispersion calculated in this way is only partially dependent on theory. Its relation to the dispersion required by a purely theoretical calculation may be ascertained by considering the relation of the observed intensity of absorption to the theoretical value calculated from the quantum-mechanical value of the oscillator strength. The latter has already been discussed by Stobbe,[*] and will be further considered here from the present standpoint.

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* 'Ann. Physik,' vol. 72, p. 585 (1927).

† [*Note added in proof, November* 20, 1933.—Since this paper was communicated for publication, a paper, on the dispersion of X-rays, by H. Hönl has appeared (Z. Physik, vol. 84, 1933). Two of the main problems considered here are also dealt with by Hönl, with similar results. One is the equivalence of 2 K electrons to about 1·3 classical electrons. The explanation given here for this experimental result is essentially the same as Hönl's, though presented in a somewhat different way. The other is the calculation of the dispersion for electrons whose photoelectric absorption obeys other laws than $\mu \propto \lambda^3$. Hönl considers the dispersion corresponding to $\mu \propto 4x^3 - x^4$, where $x = \lambda/\lambda_0$, λ_0 being the absorption edge. In the present paper we consider the dispersion for $\mu \propto x^{2\cdot 5}$, and $\mu \propto x^{3\cdot 0}$. Hönl's law, *viz.* $\mu \propto 4x^3 - x^4$, is, for $x \simeq 1$, approximately equivalent to $\mu \propto x^{2\cdot 7}$.]

The virtual oscillators associated with an atomic electron consist of two classes, viz., a discrete series of oscillators with frequencies corresponding to transitions of the electron to discrete states in the atom, and a continuous series of oscillators with frequencies corresponding to transitions of the electron to states of positive energy in the continuous spectrum. The anomalous dispersion of X-rays largely concerns the K electrons, and the oscillators associated with these are practically all represented by the second of the above classes. The total strength of those belonging to the first is small, on account of the fact that, except for light atoms, the more important discrete states in the atom into which the K electrons can make transitions are all occupied. The absorption data required for evaluating the oscillator strength thus mainly concern photoelectric absorption. The oscillator strength corresponding to the observed photoelectric absorption has been previously considered by several workers. It is further considered in § 2 of this paper where the strengths of the oscillators belonging to the K continuum and also the L continuum of various elements are calculated from recent absorption data.

The calculation of the dispersion from the oscillator strength may be formally based on the electromagnetic dispersion formula for a single damped oscillator. The dispersion produced by a continuum of oscillators is obtained from this formula by integration. The function to be integrated depends on how the oscillator strength varies with the natural frequency, and this is given by the variation with frequency of the photoelectric absorption which the oscillators give rise to. The simplest empirical law for the latter is $\mu \propto \nu^{-n}$ with $n = 3$, and the dispersion produced by a continuum obeying this law was considered by Kallmann and Mark (*loc. cit.*). This law of absorption is, however, not universally obeyed, and the L absorption near the L edge conforms more nearly to a value of $n = 2\cdot5$ than $n = 3\cdot0$, and for some elements a still lower value of n is required. In view of this, and also to show the general nature of the dependence on n, dispersion formulæ are also calculated in § 2 for $n = 2\cdot0$, and $n = 2\cdot5$. From the results obtained the dispersion may be interpolated for any value of n between $2\cdot0$ and $3\cdot0$. Much of the experimental work on the anomalous dispersion of X-rays has been done on iron near the K edge, and this case is therefore considered in detail. In the calculations the anomalous effect due to the L electrons is considered, as well as the main effect due to the K electrons. Allowance is also made for the phase effect recently emphasized by Coster and Knol.*

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[*] 'Ann. Physik,' vol. 7, p. 661 (1930).

§ 3 *of this paper is devoted to a discussion of the relation between the* empirical oscillator strength, *i.e.*, the strength calculated from the observed intensity of photoelectric absorption, and the theoretical value required by quantum mechanics.

§ 2. *Calculation of Dispersion from Absorption Data.*

If for a certain continuum of oscillators in an atom, df denote the resultant strength of the oscillators with natural frequency between ν and $\nu + d\nu$, and μ_ν the corresponding coefficient of photoelectric absorption of radiation of frequency ν by an atmosphere containing one atom per unit volume, then

$$df/d\nu = (mc/\pi e^2)\,\mu_\nu. \tag{1}$$

This relation is required by quantum mechanics, but was first derived by Ladenburg† on the basis of the old quantum theory and classical theory. The oscillator strength df represents the ratio of the amplitude of the wave scattered by the oscillators with frequencies between ν and $\nu + d\nu$ to the amplitude of the wave scattered by one classical electron of natural frequency ν. The latter, in terms of the amplitude scattered by a free classical electron as unity, is

$$\frac{\nu_i^2}{\nu^2 - \nu_i^2 + i\nu k}, \tag{2}$$

ν_i represents the frequency of the incident radiation, and k is a radiation damping factor. The amplitude of the wave scattered by a continuum of oscillators with natural frequencies extending from $\nu = \nu_0$ to $\nu = \infty$, in terms of the above unit, is therefore

$$\mathrm{F} = (mc/\pi e^2)\int_{\nu_0}^{\infty} \frac{\mu_\nu \nu_i^2}{\nu^2 - \nu_i^2 + i\nu k}\, d\nu. \tag{3}$$

On account of the damping factor, k, F is complex. The real part of it represents the amplitude, F′, of the waves scattered in phase with the incident waves, and the imaginary part the amplitude, F″, of waves scattered with a phase difference of $\pi/2$ from that of the incident waves. k has the dimensions of frequency. Its magnitude is of the order of the width of spectrum lines, and is therefore very small compared with the frequency ν of the virtual oscillators. By virtue of this, and also provided μ does not vary appreciably for a variation of frequency of the order of k, *i.e.*, provided $(k/\mu)\,d\mu/d\nu$ is small—the scattered amplitudes are practically independent of the value of k, and for radiation of frequency ν_i they are approximaely represented by

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* 'Proc. Roy. Soc.,' A, vol. 139, p. 459 (1933).

† 'Z. Physik,' vol. 4, p. 451 (1921).

$$\mathrm{F}' = (mc/\pi e^2)\int_{\nu_0}^{\infty} \mu_\nu \nu_i^2\, d\nu/(\nu^2 - \nu_i^2) \qquad (4)^*$$

$$\mathrm{F}'' = (mc/2e^2)\,\mu_{\nu_i}\nu_i. \qquad (5)^*$$

The fact that k does not appear in these expressions means that F′ and F″ can be directly evaluated from a knowledge of the photoelectric absorption coefficient, μ. We shall now consider the experimental data for the latter. If we assume that the value of μ for a continuum of oscillators obeys

$$\mu_\nu \propto \nu^{-n} = \mathrm{A}\nu^{-n},$$

then for that continuum the absorption may be completely described by three parameters, such as n, A and the frequency limit ν_0 of the continuum. This simple power law is obeyed with sufficient accuracy in actual cases that the corresponding representation may be used without introducing any serious error. Table I gives on this basis the distribution of photoelectric absorption for the K and L continuums of a number of elements. The three parameters actually chosen are λ_0, μ_0 and n; λ_0 being the wave-length corresponding to ν_0, and μ_0 the value of μ at $\nu = \nu_0$. Allen's[†] and Jönsson's[‡] absorption data were used in computing the values of n and μ_0. The values of n in the table actually represent the variation of μ from ν_0 to about $2\nu_0$, because in all cases the greater part of the oscillator strength lies within this region of natural frequency. For the L continuum there are three absorption edges, and the

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[*] The errors involved in these expressions are appreciable only for radiation of frequency, ν_i, very close to the absorption edge ν_0—the condition $(k/\mu)d\mu/d\nu \ll 1$ not being satisfied at the edge where μ suddenly falls to zero. For radiation of frequency ν_i differing from ν_0 by an amount large compared with k, the error is small and is quite negligible on the long wave-length side of ν_0. On the short wave-length side it may, however, not be wholly insignificant even though $\nu_i - \nu_0$ may be appreciably greater than k. This has been shown by Glocker and Schafer who evaluated the exact expression (3) in certain special cases, assuming various values for k. The exact evaluation of the small correction in this region must await a quantum-mechanical treatment of the value of k for a continuous spectrum.

[†] 'Phys. Rev.,' vol. 27, p. 266 (1926); vol. 28, p. 907 (1928).

[‡] "Inaugural Dissertation, Uppsala University" (1928).

values of λ_0 and μ_0 given in the table are effective mean values. In estimating the absorption by the K and L electrons from the experimental results, allowance is made for absorption by electrons in higher energy levels. The total oscillator strength, f, is also given in the table. From (1)

$$f = (mc/\pi e^2) \int_{\nu_0}^{\infty} \mu_\nu \, d\nu = (mc^2/\pi e^2)\, \mu_0/\lambda_0\, (n - 1). \tag{6}$$

Table I.—Empirical Oscillator Strength of K and L Continuums.

Element.	Continuum.	$\lambda_0 \times 10^8$.	$\mu_0 \times 10^{20}$.	n.	f.	f per electron.
Al (13)	K	7·95	15·7	2·6	1·40	0·70
Fe (26)	K	1·74	3·91	2·75	1·45	0·72
Cu (29)	K	1·38	2·80	2·70	1·35	0·67
Ag (47)	K	0·484	1·08	2·96	1·29	0·64
Cu (29)	L	12·5	750	2·3	5·2	0·67
Ag (47)	L	3·4	30	2·4	5·6	0·70
Pb (82)	L	0·88	8·2	2·6	5·0	0·62

The general formula (4) for the scattered amplitude F′ was evaluated by Kallmann and Mark for $n = 3$. The values of n for some of the elements represented in the above table, however, differ appreciably from 3, and in view of this the expressions for F′ for $n = 2\cdot0$ and $n = 2\cdot5$ have also been calculated. The following are the formulæ obtained for these values of n, together with that for $n = 3$ and also the formula for a single oscillator :—

$\underline{n = 2\cdot0}$

$$F' = f\left\{1 - \frac{1}{2x}\log\frac{x+1}{|x-1|}\right\} \tag{7}$$

$\underline{n = 2\cdot5}$

$$F' = f\left\{1 + \frac{3}{2x^{3/2}}\left(\pi/2 - \cot^{-1} x^{\frac{1}{2}} - \tfrac{1}{2}\log\frac{x^{\frac{1}{2}}+1}{|x^{\frac{1}{2}}-1|}\right)\right\} \tag{8}$$

$\underline{n = 3\cdot0}$

$$F' = f\left\{1 + \frac{1}{x^2}\log|x^2 - 1|\right\} \tag{9}$$

single oscillator

$$F' = f\,\frac{x^2}{x^2 - 1}. \tag{10}$$

$x = \nu_t/\nu_0$; $f =$ total oscillator strength (given by (6)).

The variation of F′ with ν_i in the neighbourhood of $\nu_i = \nu_0$ (*i.e.*, $x = 1$) for the different values is represented graphically in fig. 1. For a single oscillator (curve D) $F' \to f$ as $x \to \infty$, and $F' \to 0$ as $x \to 0$. These general features are necessarily reproduced by each of the continuums, but there are appreciable differences in their behaviours between these extremes. For a single oscillator, as x decreases from large values, F′ increases, and approaches $+\infty$ as x approaches 1. For the continuums with $n = 2\cdot5$ (curve B) and $3\cdot0$ (curve C), F′ also increases with decreasing x at the start, and somewhat more rapidly than for a single oscillator. That there is an initial increase at all means that there is a sufficient concentration of oscillator strength near $\nu = \nu_0$ so that the increase in F′ owing to the approach of ν_i to this region more than balances the negative contribution from the oscillators whose frequencies exceed ν_i. For smaller x, *i.e.*, smaller ν_i, this ceases to be so, and at the points p the excess anomalous scattering due to the oscillators with $\nu < \nu_i$, $= \nu_p$, is exactly balanced by the negative anomalous scattering from the oscillators with $\nu > \nu_p$. For radiation of frequency $\nu_i < \nu_p$ the negative contribution from the oscillators with $\nu > \nu_i$ more than balances the excess positive contribution from those with $\nu < \nu_i$, and for $\nu_i < \nu_q$ F′ is negative. For $n = 2\cdot0$ (curve A) the oscillator

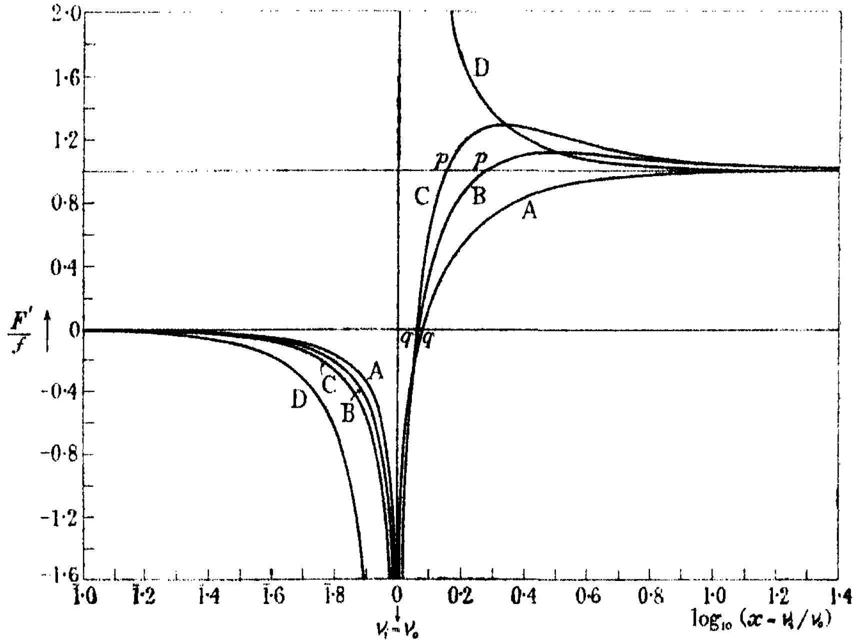

FIG. 1.—Anomalous scattering for continuum obeying $df/d\nu \propto \nu^{-n}$. $n = 2\cdot0$, curve A; $n = 2\cdot5$, curve B; $n = 3\cdot0$, curve C; ν_0 = frequency of the edge of the continuum. ν_i = frequency of radiation. Ordinates represent scattered amplitude F′, in terms of resultant oscillator strength, f, of continuum. D represents F′ for single oscillator of frequency ν_0, strength f.

strength is sufficiently dispersed so that for all ν_i the negative contribution from oscillators with $\nu > \nu_i$ is greater than the excess positive contribution from those with $\nu < \nu_i$, so that F′ is less than the asymptotic value, *f*, for all ν_i.

It is of interest to notice that the curves B and C, corresponding to $n = 2{\cdot}5$ and $n = 3{\cdot}0$ respectively, pass through their maxima at the points where they cut the curve D, for a single oscillator. This is not an accidental circumstance for these particular values of *n*, but is a general property for all *n* which give a maximum. To prove this we take the general expression for F′, viz.,

$$\mathrm{F}' = (mc/\pi e^2) \int_{\nu_0}^{\infty} \mu \, d\nu/(1 - \nu^2/\nu_i^2)$$

$$= (mc/\pi e^2)\, \mu_0 \nu_0^{\,n} \nu_i^{-(n-1)} \int_{y_0 = \nu_0/\nu_i}^{\infty} y^{-n} (1 - y^2)^{-1} \, dy. \qquad (11)$$

At the point where the variation of F′ with ν_i passes through a maximum $\partial \mathrm{F}/\partial \nu_i = 0$, *i.e.*,

$$-(n-1)\, \nu_i^{-n} \int_{\nu_0/\nu_i}^{\infty} y^{-n} (1 - y^2)^{-1} \, dy + \nu_i^{-(n-1)} (\nu_0/\nu_i^2)\, y_0^{-n} (1 - y_0^2)^{-1} = 0$$

$$(n-1)\, y_0^{(n-1)} \int_{\nu_0/\nu_i}^{\infty} y^{-n} (1 - y^2)^{-1} \, dy = (1 - y_0^2)^{-1}.$$

By virtue of (6) and (11), and the identity of $y_0 = \nu_0/\nu_i$ with x^{-1} in equations (7)–(10), this reduces to

$$\mathrm{F}' = f/(1 - x^{-2}),$$

where *f* is the resultant oscillator strength of the continuum. The right-hand side is the value of F′ for a single oscillator of frequency ν_0 and strength *f*. The value of F′ for a continuum therefore passes through a maximum where its value is equal to that for a single oscillator, whose natural frequency coincides with the edge of the continuum and whose strength is equal to the resultant strength of the continuum.

On the long wave-length side of the edge of the continuums, *i.e.*, $\nu_i < \nu_0$, $x < 1$, all the oscillators give a negative contribution, so that the resultant amplitude F′ is necessarily negative. For a given value of ν_i/ν_0 the absolute value of F′ is greater the greater the value of *n*, which is understandable because the greater *n* the nearer is the "centre of gravity" of the continuum to ν_0, and therefore the nearer it is to ν_i. For $\nu_i \ll \nu_0$ the equations (7)–(9) reduce to

$$\mathrm{F}' = f \,.\, (n-1)/(n+1) \,.\, \nu_i^2/\nu_0^2,$$

which is the same as the limiting formula for a single oscillator of strength f and natural frequency $\nu_0 \times (n+1)^{\frac{1}{2}}/(n-1)^{\frac{1}{2}}$. Thus for very small frequencies a continuum of oscillators obeying $df/d\nu \propto \nu^{-n}$ is equivalent to a single oscillator of the same resultant strength, and frequency equal to $\nu_0 \times (n+1)^{\frac{1}{2}}/(n-1)^{\frac{1}{2}}$. The latter may accordingly be regarded as the "centre of gravity" of the continuum.

As regards the infinite values given by the formulæ (7)-(10) at $\nu_i = \nu_0$., *i.e.*, $x = 1$, we recall that (4) ceases to be valid when ν_i is very close to ν_0. An evaluation of the exact formula (3) does not, of course, make F′ infinite at $\nu_i = \nu_0$. The error in (4), owing to the approximation it involves, takes place too close to ν_0 to affect perceptibly the curves in fig. 1, and it is of little consequence to the present applications.

As regards the direction of scattering, if the linear scale, σ, of the distribution in space of the charge associated with the virtual oscillators, is comparable with, or greater than, the wave-length λ_i, of the incident radiation, then, except for small angles of scattering, there is appreciable destructive interference between the radiation scattered from different parts of the oscillating charge. Under these conditions the values of F given by the above equations hold only for scattering in the forward direction. However, in the region of anomalous scattering λ_i is of the order of λ_0, whilst in all cases $\sigma \ll \lambda_0$.[*] It follows that in this region of wave-length there is no interference effect, and the amplitude of the scattered wave is represented by the above equations for all directions of scattering.[†]

A number of experiments have been made on the anomalous dispersion of X-rays. We shall consider the results of those in which the atomic scattering power of an element is obtained by observing the intensity of reflection of X-rays by a crystal containing that element. Experiments of this kind have been carried out by Wyckoff,[‡] Glocker and Schafer,[§] Bradley and Hope,[||] and Rusterholz.[¶] The quantity observed in these experiments is the amplitude,

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[*] For the K continuum, for example, the scale, σ, of the space distribution associated with the oscillators is of the order of a/Z, where a is the radius of the hydrogen atom, and Z is the atomic number. λ_0 in this case is of the order of the K characteristic wave-lengths $\sim \lambda_H/Z^2$, where λ_H is the limit of the Lyman series of hydrogen $\sim$ 1000 A. The ratio of λ_0 to σ is therefore of the order of $(\lambda_H/Z^2)/(a/Z) \sim 2000/Z$, which is large for all elements.

[†] The absence of interference also means that there are no complications due to Compton scattering.

[‡] 'Phys. Rev.,' vol. 35, pp. 215, 583 (1930); vol. 36, p. 1116 (1930).

[§] 'Z. Physik,' vol. 73, p. 289 (1931).

[||] 'Proc. Roy. Soc.,' A, vol. 136, p. 272 (1932).

[¶] 'Z. Physik,' vol. 82, p. 538 (1933).

F_a, of the the wave scattered by a whole atom of the element. The contribution of the outer atomic electrons to F_a varies with the angle of scattering on account of the interference effect referred to in the previous paragraph. For a given value of $\sin\theta/\lambda_i$, where 2θ is the angle of scattering and λ_i is the wave-length of the radiation, the interference effect is, however, constant, and a variation of F_a with λ_i under these conditions must be attributed to anomalous dispersion. The most accurate results obtained by Bradley and Hope refer to a value of $\sin\theta/\lambda_i = 0{\cdot}3$. The observed variations of F_a with λ_i for this value of $\sin\theta/\lambda_i$ are given in Table III, together with the calculated values. The results are given in terms of departures from the value of F_a for the shortest wave-length used in the experiments, viz., 0·71 A.

The contribution of different sources to the calculated values for iron are given in Table II. The third column of this table gives the contribution to F'_a from the K continuum. This is calculated from the oscillator strength given in Table I, using the formulæ which give the values of F' for different values of the exponent n in the law $\mu \propto \lambda^n$. For the K continuum of iron $n = 2{\cdot}75$. Though no appreciable error would be entailed by taking $n = 3$, the values given here have been computed for $n = 2{\cdot}75$, by interpolation from the values given by the formulæ (8) and (9) for $n = 2{\cdot}5$ and $n = 3{\cdot}0$ respectively. The fifth column of Table II gives the contribution to F'_a from the L continuum.* Owing to lack of data for the L photoelectric absorption by iron, the L oscillator strength has been assumed to be the same as that for the neighbouring element copper, for which the L absorption has been fully investigated by Jönsson, with the results given in Table I. The L anomalous effect is sufficiently small that any errors due to this assumption are quite insignificant. The effect is indeed so small that it could almost be completely neglected, and it is considered here more to show that it *is* small than to make an allowance for it.

The contribution, $\delta F''_a$, to F_a, due to waves scattered at a phase difference of $\pi/2$ from the incident waves, is given in the fifth column. If F''_a denote the amplitude of these waves for the whole atom, F'_a the amplitude of the waves scattered in phase with the incident waves, then by $\delta F''_a$ we mean $(F'^2_a + F''^2_a)^{\frac{1}{2}} - F'_a$. From (5) F''_a is given by

$$F''_a = (mc^2/2e^2)\mu_a/\lambda_i, \tag{11}$$

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* The interference factor for the L electrons is sufficiently constant that its decrease with scattering angle can be completely neglected so far as the small variation in F due to anomalous dispersion is concerned.

where μ_a is the absorption coefficient of the whole atom for radiation of wave-length λ_i. The last column of Table II gives the resultant variation in F_a, being the sum of the variation in the values of F'_K, F'_L and $\delta F''_a$. The numbers given represent departures from the value of F_λ for $\lambda_i = 0 \cdot 71$, in accordance with Table III. The results are represented graphically in fig. 2 (*a*). Rusterholzes

Tables II and III.—Anomalous Dispersion of X-rays by Iron.

Table II.

λ_i (A.).	K continuum $\lambda_K = 1 \cdot 738$ A.		L continuum $\lambda_L = 17 \cdot 2$ A.		$\delta F''$.	$F_{\lambda_i} - F_{0 \cdot 71}$.
	$x_K = \lambda_K/\lambda_i$.	F'_K.	$x_L = \lambda_L/\lambda_i$.	F'_L.		
0	∞	1·45	∞	5·20	0	−0·4
0·71	2·45	1·75	24·2	5·27	0·02	(0·0)
1·54	1·13	−0·13	11·1	5·42	0·38	−1·3
1·66	1·05	−1·45	10·4	5·43	0·65	−2·4
1·725	1·01	−3·65	10·0	5·44	0·93	−4·3
1·755	0·99	−3·87	9·8	5·45	0·02	−5·5
1·83	0·95	−2·06	9·4	5·45	0·02	−3·6
1·79	0·97	−2·60	9·6	5·45	0·01	−4·2
1·93	0·90	−1·39	8·9	5·47	0·02	−2·9
2·27	0·77	−0·68	7·6	5·53	0·03	−2·2
4·4	0·40	−0·12	4·0	5·77	0·35	−1·1

Table III.

λ_i (A.).	$x_K = \lambda_K/\lambda_i = 1 \cdot 74/\lambda_i$.	$F_{\lambda_i} - F_{0 \cdot 71}$ (calculated).	$(F_{\lambda_i} - F_{0 \cdot 71})$ observed by		
			Bradley and Hope.	Glocker and Schafer.	Wyckoff.
0·71	2·45	(0·0)	(0·0)	(0·0)	(0·0)
1·54	1·13	−1·3	−0·5	−5·5	−4·5
1·79	0·97	−4·2	−3·1	—	—
1·93	0·90	−2·9	−1·5	−3·6	−2·5
2·17	0·77	−2·2	−0·0	—	—

results for copper and the calculated values for this element are represented in fig. 2 (*b*). Rusterholz did not make observations on the short wave-length side of the absorption edge and the ordinates in this figure represent departures from the theoretical *normal* scattering amplitude.

The experimental values of F_a in the neighbourhood of the K absorption edge are less than elsewhere, and in this respect they are in qualitative agreement with the calculated values. The effect under consideration concerns changes in F which are small compared with the total value of F, and accurate quantitative agreement is not to be expected. As regards the actual differences, the results obtained by different observers do not show a consistent departure from the calculated values. On the short wave-length side of the absorption edge, at the point $\nu_i/\nu_0 = 1\cdot13$, the calculated value of F is only about 1 unit less than at $\nu_i/\nu_0 = 2\cdot45$. The observed decrease in F in this region according to Wyckoff, and Glocker and Schafer, is much greater, being about 5 units. The decrease observed by Bradley and Hope is, however, in fair agreement with the calculated value, being actually somewhat less. The results obtained by Bradley and Hope on the long wave-length side of the

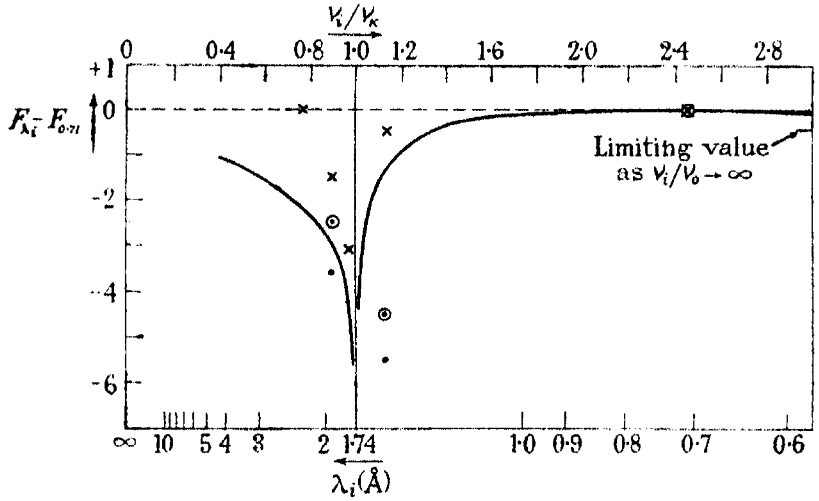

FIG. 2 (*a*).—Anomalous scattering by iron. — calculated; × Bradley and Hope • Glocker and Schafer; ⊙ Wyckoff.

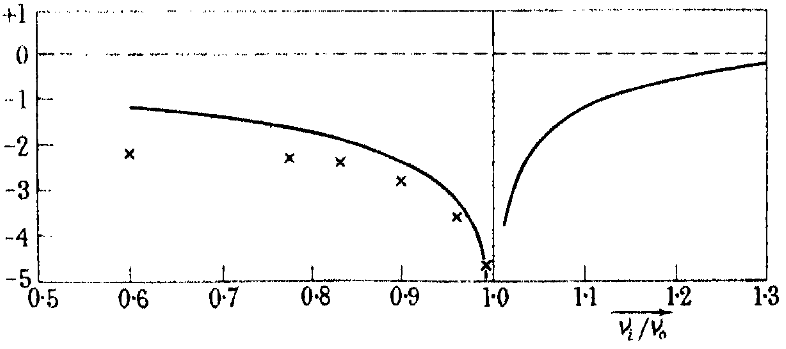

FIG. 2 (*b*).—Anomalous scattering by copper. — calculated; × Rusterholz.

edge are not in as good agreement with the calculated values. They find that in this region F returns to its value for short wave-lengths, whilst the calculated values do not do so.* In this respect the calculated values are, however, satisfactorily borne out by the experimental results obtained by Rusterholz for copper, fig. 2 (*b*). Rusterholzes values actually show a smaller rise in F as ν_i/ν_0 decreases from unity than the calculated rise. The calculated values are, of course, subject to some measure of error owing to the possible errors in the absorption data used to calculate the oscillator strength, the numerical errors in the calculation of the scattering from the oscillator strength, and also the assumption that k in (4) is negligible compared with ν_0. The resulting possible error in the calculated departures of F from its normal value is, however, not more than about 10%.

A point of interest in connection with the above experimental determinations of the anomalous scattering by a given element is the assumption that the scattering by another element, used as a standard of comparison, is normal. The error incurred by this assumption is small, though not wholly insignificant. In the experiments on iron, for example, the scattering by aluminium is assumed to be normal in the region of wave-length concerned. From Table I the wave-length of the K edge of Al is 8 A., the K oscillator strength is 1·4 units, and n is 2·6. Using these data and the formulæ (8) and (9) for F′ for $n = 2\cdot5$ and 3·0, we find that the value of F_a for Al increases by 0·13 units as λ_i decreases from 0·71 to 2·2 A.—the range investigated by Bradley and Hope. The value of F for an aluminium atom in the directions concerned in the experiments of the latter is about half of that for an iron atom. It follows that the variation in the value of F for iron for the above wave-length range is the value calculated assuming Al to be normal, *plus* $2 \times 0\cdot13 \sim 0\cdot3$. This is small compared with the actual anomalous effect which for certain wave-lengths is of the order of 2 to 3 units. Inasmuch as it has an effect it raises the experimental values of F for iron for large wave-lengths.

§ 3. *Theoretical Oscillator Strength.*

The calculation of the dispersion in the previous section is based on the distribution of oscillator strength deduced from the observed intensity of photoelectric absorption. In this section we shall consider briefly the relation of this empirical oscillator strength to theoretical requirements.

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* This theoretical result is independent of any detailed assumption made about the distribution of oscillator strength in the K continuum, and represents a well-established feature of dispersive scattering, viz., that the phase of the waves scattered by an undamped oscillator changes by π as the frequency of the radiation changes from a value greater than the natural frequency of the oscillator to a value less than that frequency.

According to the summation law of Thomas and Kuhn the resultant strength of the oscillators associated with an atomic electron, in terms of 1 classical electron as unity, is one. The oscillators associated with the 2K electrons in an atom are practically all represented by the K continuum. We would therefore, on the basis of the above law, expect the latter to have an oscillator strength of 2 units. This value is in fact assumed by Kallmann and Mark in their treatment of dispersion. It is, however, appreciably greater than the empirical value, which is in the neighbourhood of 1·3. A qualitative explanation of this deficit has been given by Kramers and Kronig.* The summation law as stated above refers only to single electron systems. For an atom with many electrons the law only requires the total oscillator strength of the whole atom to be equal to the number of electrons in it. So far as the electrons in an atom with many electrons may be treated separately, the summation law may, however, still be applied to individual electrons, or groups of electrons, in the atom, provided we take into account the oscillators corresponding to transitions of the electrons concerned, not only to states in the atom which are not occupied, but also to the occupied states.† For the K electrons, for example, we must include the strength of the oscillators corresponding to transitions of the K electrons to the occupied L, M levels, etc., with that of the K continuum in order to obtain a total of 2. For the K electrons all possible transitions are to states of greater energy so that the strengths of all the oscillators have the same sign. The strength of the K continuum is therefore of necessity less than 2. As regards the actual value Kramers and Kronig show that if a K electron behaved like a hydrogen-like electron in the ground state the strength of the K continuum would be 0·87 units. This is appreciably less than the empiricial value of about 1·3, and it is to this divergence from hydrogen-like values that we wish to pay particular attention in this section. According to Kramers and Kronig the K electrons are so near being hydrogen-like that the divergence from 0·87 should be very small, and no explanation is given of the actual discrepancy of about 60%.

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* 'Z. Physik,' vol. 48, p. 174 (1928).

† Taking into account all the virtual oscillators in the atom precluded by the exclusion principle does not give a wrong oscillator strength for the whole atom. This is so because the oscillators thus introduced cancel out in pairs. One oscillator in a pair corresponds to a transition from an occupied state n to an occupied state m, and the other to the reverse transition. The resultant strength of a pair is zero because the strength of an oscillator nm is equal but opposite in sign to that of the oscillator mn—they give scattered waves equal in amplitude but differing in phase by π.

In quantum mechanics the oscillator strength is intimately connected with the wave functions which represent the different states of the atom. If an atomic electron is in a state represented by a wave function ψ_n, with proper energy E_n, then the strength, f, of a virtual oscillator of frequency, ν, associated with the electron, is proportional to

$$|q_{nm}|^2 = \left|\int q\psi_n\bar{\psi}_m\,d\tau\right|^2, \tag{13}*$$

where q is a Cartesian co-ordinate, and ψ_m represents a state of the electron with proper energy $E_n + h\nu$. If the state m belongs to the continuous spectrum then $|q_{nm}|^2$ represents the strength per unit frequency range, $df/d\nu$, of the oscillators with frequency ν. Owing to analytical difficulties an exact evaluation of the matrix element q_{nm} is not possible except for the simplest case of a hydrogen-like atom. In all other cases approximations have to be made. For the K continuum the matrix element concerned is

$$q_{K,m} = \int q\psi_K\psi_m\,d\tau, \tag{14}$$

where ψ_K is the wave function for the K electron in the K level, and ψ_m is the wave function for a K electron excited to a state in the continuous spectrum. Except in very light atoms the K electrons are confined to a region where the field is practically Coulombian. ψ_K is, therefore, very nearly the same as the wave function for a hydrogen-like atom in the ground state, provided we give the latter an appropriate nuclear charge. According to an estimate by Slater the best effective nuclear charge for ψ_K is $(Z - 0{\cdot}3)e$, where Z is the atomic number. The possible error in this approximation to ψ_K corresponds to an error in the nuclear charge of no more than a fraction of e. For Cu, *e.g.*, Z is 29, so that the error here corresponds to a change in Z of only about 1%. q_{Km} depends on the excited state ψ_m as well as the initial state ψ_K. Since m is a state of positive energy, the corresponding wave function ψ_m decreases comparatively slowly with increasing distance from the nucleus. It will, therefore, not be negligible in the regions occupied by the L and outer electrons, and in these regions the effective nuclear charge differs appreciably from $Z - 0{\cdot}3$. Since, however, q_{nm} depends on the product of ψ_K and ψ_m it is only the values of ψ_m in the region where ψ_K is appreciable that matters. The *variation* of

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* Strictly speaking this should be written as $\Sigma\left|\int q\psi_n\bar{\psi}_{m,s}\,d\tau\right|^2$, $\psi_{m,s}$ representing state of energy $E_n + h\nu$, and Σ_s denoting summation over all such states.

ψ_m in this region depends only on the field in this region, and the total energy $E_K + h\nu$. Apart from an effect on the normalizing factor we would, therefore, expect ψ_m, so far as its value in q_{Km} is concerned, to correspond to the same effective nuclear charge as ψ_K, viz., $Z - 0{\cdot}3$. In other words we would expect a K oscillator of given frequency to have a strength approximately equal to that of a hydrogen-like atom of nuclear charge $(Z - 0{\cdot}3)e$. Stobbe (*loc. cit.*) has made calculations of the K photoelectric absorption—which is a direct measure of the oscillator strength—on the assumption of this effective nuclear charge, and finds satisfactory agreement with experiment. Observed and calculated values for a few elements are given in Table IV.

Table IV.

Element.	λ_K (A.).	Wave-length of absorbed radiation (A.).	μ_K/ρ.	
			Observed.	Calculated on assumption of $Z_{\text{Effective}} = Z - 0{\cdot}3$.
Cu	1·38	1·090	144	142
Cu	1·38	0·709	45	46
Cu	1·38	0·430	10·6	10·5
Ag	0·48	0·417	36	32
Al	7·95	5·65	1540	1750

The table shows that the variation of μ with wave-length is well represented by the hydrogen-like formula, and that the absolute values are also given within about 10%. The actual oscillator strength in the K continuum is therefore equal, within about 10%, to the theoretical oscillator strength in the continuum of a hydrogen-like atom in the ground state, with nuclear charge $(Z - 0{\cdot}3)e$. The difference which does exist is probably due to the effect of the L and outer electrons on the normalizing factor for ψ_m in (14). The question then is, why does the *resultant* oscillator strength of the K continuum differ by about 60% from that of a hydrogen-like atom ? The answer is that though the L and outer electrons in the atom little affect the strength of an oscillator of given frequency, they cause an appreciable extension of the K continuum into the region of low frequencies. The theoretical frequency ν'_K of the absorption edge for a hydrogen-like atom of nuclear charge $(Z - 0{\cdot}3)e$ is $(Z - 0{\cdot}3)^2R$, where R is Rydberg's constant. The actual frequency ν_K of the K absorption edge is appreciably less than this, being approximately equal to $(Z - 3)^2R$. The theoretical oscillator strength of the K continuum is therefore approximately equal to that of the continuum of a hydrogen-like atom in the ground state, viz., 0·87, ***plus* that** of the oscillators with frequencies between ν'_K and ν_K. Owing to the **large** intensity of the oscillator strength near the absorption edge, the **latter is** sufficient to account for the 60% excess of the actual oscillator strength over 0·87. The case of copper is represented in detail in fig. 3.

The crosses represent the observed K photoelectric absorption.* The **curve** ECD represents the theoretical absorption assuming the K electrons to **be**

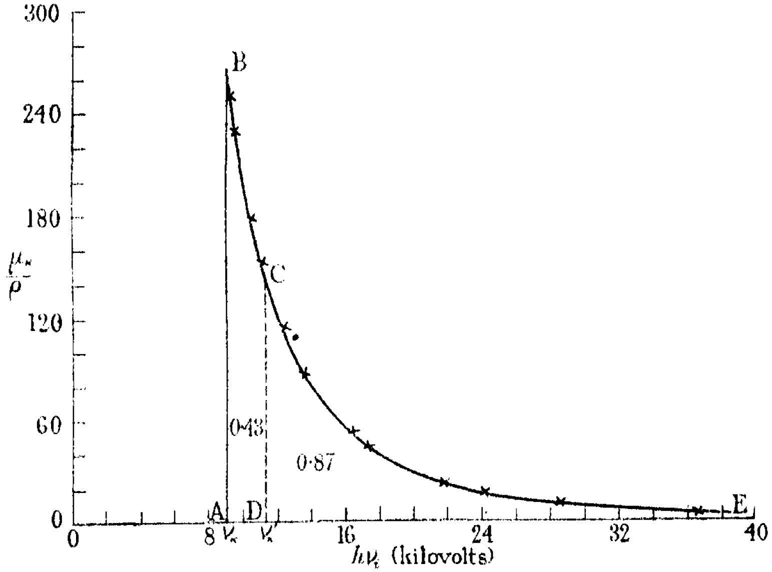

FIG. 3.—K photoelectric absorption by copper. C—E theoretical, assuming hydrogen-like wave function $Z_{eff.} = Z - 0{\cdot}3$; B—C extrapolation of EC; × observed by Allen and Jönsson.

hydrogen-like with effective nuclear charge of $(Z - 0{\cdot}3)e$. The frequency ν'_K is the corresponding absorption edge $= (Z - 0{\cdot}3)^2 R$. ν_K is the actual absorption edge of the K electrons $\sim (Z - 3)^2 R$. CE approximately corresponds to the law $\mu \propto \lambda^{2\cdot8}$, and CB is an extrapolation of the theoretical curve CE on the basis of this law. The area under CE represents the oscillator strength of the continuum of a truly hydrogen-like atom, viz., 0·87. ABCD represents the excess over this value of the oscillator strength of K electrons, caused by the displacement of the K edge by the L and outer electrons. Its area corresponds to 0·43 units, giving a total oscillator strength of 1·30, as compared with 1·32 units, which is approximately the area under the observed points. This degree of agreement is rather exceptional, and in general the resultant oscillator strength obtained by extrapolating the hydrogen-like formula to the actual K edge as in the above figure, and which is given by

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* Equal to 7/8 of the total absorption by the atom.

$$f_K = 0\cdot 87\,(\nu'_K/\nu_K)^{1\cdot 8}, \tag{15}$$

represents the oscillator strength of the K continuum only within about 10%. Differences of this order are, however, not unexpected. The main point which it is desired to bring out here is that the *bulk* of the excess of the K oscillator strength over the hydrogen-like value of 0·87, is accounted for by the extension of the K continuum caused by the shielding effect of the L and outer electrons.

It is of interest to observe that the excess of the strength of the K continuum over the hydrogen-like value requires that the strength of the discrete K oscillators—corresponding to transitions of the K electrons to discrete levels in the atom, occupied and unoccupied—must by the summation law be less than the hydrogen-like value by nearly the same amount. A general explanation of this follows from the fact that the oscillator strength, per unit frequency range, of the discrete oscillators of a hydrogen-like atom near the frequency limit, ν_0, of the series, is the same as that of the continuous spectrum at ν_0. This continuity in the oscillator strength, as we pass from the continuous to the discrete spectrum, means that the increase in the strength of the former by a displacement of the K edge must, at least approximately, be accompanied by an equal decrease in the latter. The resultant oscillator strength is accordingly conserved.

In his calculations on photoelectric absorption Stobbe also considered the L electrons. He assumes them to behave like hydrogen-like electrons with a total quantum number of 2, and a nuclear charge equal to $(Z - 4\cdot 14)e$. This assumption for the L electrons is much less accurate than the corresponding assumption for the K electrons. Even so it gives moderate agreement with the observed absorption for certain elements, for wave-lengths small compared with the wave-length at the L edge. However, for moderately heavy elements, such as copper, and wave-lengths near the L edge—a case not considered by Stobbe—the values calculated on this basis differ considerably from the actual values. Data for the latter are available through recent work by Jönsson (*loc. cit.*) on the absorption of long wave-length X-rays. Stobbe's calculated L absorption and the observed L absorption for copper are represented in fig. 4. In deducing the latter from the absorption by the whole atom allowance has been made for the absorption by the M and outer electrons.

DEF represents the theoretical L absorption assuming equivalence to hydrogen-like electrons with nuclear charge $(Z - 4\cdot15)e$. ν'_L is the corresponding L edge $= \frac{1}{4}(Z - 4\cdot15)^2 R$. The crosses represent the observed absorption. The actual L edge is complex, and $\bar{\nu}_L$ in the figure is an average value.

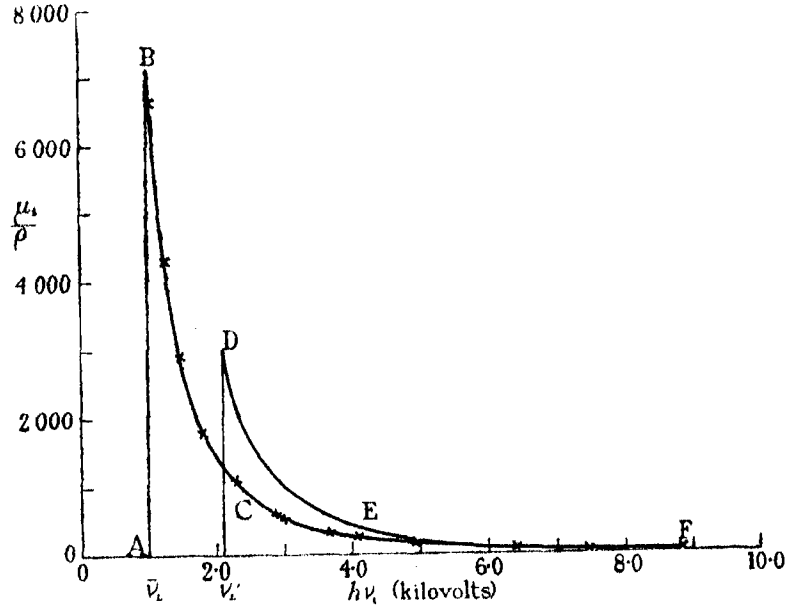

Fig. 4.—L photoelectric absorption by copper, DEF theoretical, assuming hydrogen-like wave functions, $Z_{\text{eff.}} = Z - 4\cdot15$, × observed by Jönsson.

The theoretical resultant oscillator strength of hydrogen-like L electrons is represented by the area under DEF, and by integration of Stobbe's results we find

$$f_L{}^H = \int_{\nu'_L}^{\infty} (df/d\nu)_L{}^H \, d\nu = 3\cdot0.$$

The actual oscillator strength of the L continuum of copper (as also that of other elements represented in Table I) is about 5. There is no simple relation between this experimental value and the hydrogen-like value—such as exists for the K continuum (equation (15)). It will be noticed from the figure that the slope of the hydrogen-like curve is greater than that of the experimental curve—the former corresponds to $n = 3\cdot0$, the latter to $n = 2\cdot3$. This means that the effective nuclear charge increases with increasing frequency of the oscillators,* thus counter-balancing to some extent the rapid decrease in absorption with increasing frequency. This increase in the effective nuclear charge with increasing frequency of the oscillators is to be expected, because the greater the frequency of the oscillators the less extended from the nucleus is the charge associated with them, and hence the less the shielding by outer electrons.

Before concluding we shall briefly consider the strength of the discrete oscillators corresponding to transitions of inner electrons to *unoccupied* discrete states in the atom. These oscillators must be distinguished from those corresponding to transitions to occupied states. The latter must be included in applying the summation law, but are actually not in operation. The former are operative, but in the calculations of the dispersion by iron and copper in § 2 their strength is assumed to be negligible. In estimating their theoretical strength we shall assume that the continuity in the oscillator strength per unit frequency range as we pass from the continuous spectrum of oscillators to the discrete spectrum, is true in general. Then if $\delta\nu$ represents the range of frequency of the discrete oscillators concerned, their effect on the dispersion of radiation of frequency ν_i, differing from ν_0 by appreciably more than $\delta\nu$, is approximately equivalent to that of a decrease in the frequency limit of the continuum from ν_0 to $\nu_0 - \delta\nu$. The effect of this on the anomalous dispersion is approximately measured by $\delta\nu/|\nu_i - \nu_0|$. $h\delta\nu$ is in general of the order of optical excitation potentials $\sim$ 10 volts. In the actual cases for iron considered in § 2, the smallest value of $|\nu_i - \nu_0|$ corresponds to about 300 volts. This gives $\delta\nu/|\nu_i - \nu_0| \sim 0{\cdot}03$. The effect is therefore small even in this extreme case, and the comparison of theory and experiment in § 2 is not sensibly affected by the neglect of the discrete oscillators.

Summary.

The anomalous dispersion of X-rays is calculated from the experimental data for photoelectric absorption. Iron and copper are considered somewhat in detail and the results are compared with experiment. In the second part of the paper the relation between the oscillator strength calculated from the experimental data for absorption and the quantum-mechanical oscillator-strength for hydrogen-like electrons is discussed, particular attention being paid to the K continuum of oscillators, the observed strength of which is about 1·3.

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* For Cu the effective nuclear charge taken by Stobbe, viz., $Z - 4{\cdot}15$, gives fair agreement for $\lambda \sim 2{\cdot}0$ A., whilst to obtain agreement in the region of $\lambda \sim 10$ A., for example, we must take an effective nuclear charge of $Z - 10$.

Acid Catalysis in Non-Aqueous Solvents. I.—The Rearrangement of N-bromoacetanilide.

By RONALD P. BELL.

(Communicated by C. N. Hinshelwood, F.R.S.—Received August 1, 1933.)

Introduction.

Modern theoretical and experimental research upon catalysis by acids and bases has shown that catalysis in aqueous solutions is often effected not only by the hydrogen ion (*i.e.*, H_3O^+) and the hydroxyl ion, but also by any molecular species which conforms to modern definitions of acids and bases.[*] To take an example, the muta-rotation of glucose is catalysed not only by the ions H_3O^+ and OH^-, but also by undissociated acid molecules, the ammonium ion, the water molecule, amine bases, and the anions of weak acids.[†]

On the quantitative side, Brönsted[‡] has discovered an empirical relation which is of very general application in expressing the variation of catalytic power with the acidic or basic strength of the catalyst. For acid catalysis, this relation may be written

$$k_A = GK_D^x, \tag{1}$$

where k_A is the catalytic constant of the acid, K_D its electrolytic dissociation constant, and G and x constants for a given reaction, x being always less than unity.

Practically all the results obtained so far in support of the general theory of acid and basic catalysis refer to aqueous solutions. The interpretation of such results is necessarily rather complex, since a solution of an acid or a base in water will always contain several species which may be catalytically active.[§][||]

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[*] See Lowry, 'J. Soc. Chem. and Ind.,' vol. 42, p. 43 (1923); Brönsted, 'Rec. Trav. Chim.,' vol. 42, p. 718 (1923).

[†] Brönsted and Guggenheim, 'J. Amer. Chem. Soc.,' vol. 49, p. 2554 (1927); Lowry and Smith, 'J. Chem. Soc.,' p. 2539 (1927).

[‡] Brönsted and Pedersen, 'Z. phys. Chem.,' vol. 108, p. 185 (1924); Brönsted, 'Chem. Rev.,' vol. 5, p. 231 (1928). For a review of the catalyses to which this relation applies, see Kilpatrick, 'Chem. Rev.,' vol. 10, p. 213 (1932). It has been recently shown by Pedersen ('K. danske Vidensk. Selsk. Skr.,' vol. 12, No. 1 (1932)) that the isomerization of nitromethane, acetoacetic acid, and acetoacetic ester in presence of bases also falls into the same category.

[§] Brönsted, 'Trans. Faraday Soc.,' vol. 24, p. 630 (1928).

[||] Brönsted and Wynne-Jones, 'Trans. Faraday Soc.,' vol. 25, p. 59 (1928).

For other hydroxylic solvents, *e.g.*, the alcohols, very similar considerations hold good, except that we have much less knowledge of acid-base equilibria and of salt effects, which will be correspondingly higher in these solvents of lower dielectric constant. Matters are, however, in many respects much simpler in solvents such as benzene, which possess neither acidic nor basic properties. Thus it is obvious that in a solution of, *e.g.*, hydrochloric acid in benzene, there is only one constituent possessing acidic or basic properties, *i.e.*, the HCl molecule. It is thus possible to study separately the catalytic effects of uncharged molecules through any desired range of acid or basic strength.

Apart from the simplifications thus introduced, the study of acid catalysis in non-aqueous solvents has many points of intrinsic interest. Thus little is known as to whether equation (1) is valid in non-aqueous solvents, and, if so, whether we can retain the dissociation constants measured in aqueous solution as a measure of relative acid strength, or whether it will be necessary to employ measurements of acid-base equilibria in the solvents used. Another point of interest is the constancy or otherwise of the constants G and x in equation (1) when the solvent is changed.

There is very little evidence to support the existence of general acid or basic catalysis in solvents other than water. A number of investigations in alcohol solution were at one time adduced in favour of the dual theory of catalysis, but it has been shown that these conclusions were based on false assumptions.*

Brönsted and Vance† have, however, recently shown that the decomposition of nitramide in *iso*amyl alcohol solution exhibits general basic catalysis, and that there is a relation between catalytic power in *iso*amyl alcohol and basic strength in water of the same type as equation (1).

For non-dissociating solvents, there exists a large number of isolated experimental facts which may be interpreted as acid or basic catalysis, but practically no results of quantitative significance. Thus Lowry has shown that the mutarotation of nitro-camphor,‡ beryllium benzoyl-camphor, and aluminium benzoyl-camphor§ in solvents such as chloroform, ether, and ethyl acetate is extremely sensitive to the presence of acids or bases. Similarly it has been shown that the tautomeric change of acetoacetic ester|| and various diketones¶ in the pure liquid state is greatly accelerated by the presence of organic bases.

* Brönsted, 'Chem. Rev.,' vol. 5, p. 231 (1928).

† 'Z. phys. Chem.,' A, vol. 163, p. 240 (1933).

‡ Lowry and Magson, 'J. Chem. Soc.,' vol. 93, p. 119 (1907).

§ Lowry and Traill, 'Proc. Roy. Soc.,' A, vol. 132, p. 398 (1931).

|| Rice and Sullivan, 'Trans. Faraday Soc.,' vol. 24, p. 678 (1928).

¶ Moureu, 'Trans. Faraday Soc.,' vol. 24, p. 562 (1928).

In all these reactions it has proved impossible to make any accurate determinations of catalytic power, on account of the difficulty experienced in obtaining reproducible results in the pure solvent.

Brönsted and Bell* have investigated some reactions of diazoacetic ester in benzene solution which have a bearing on the problem of acid catalysis in inert solvents. The results obtained were not very accurate, but a rough parallelism was found between the catalytic powers of the acids in benzene and their dissociation constants in water.

Apart from their low accuracy, there is a more fundamental objection to the above results. Carboxylic acids in benzene are well known to be strongly associated at the concentrations employed by Brönsted and Bell. Since nothing is known of the effect of association upon catalytic power, it would be very desirable either to work over a much larger concentration range or to use a solvent in which there is less tendency to association.

The reaction studied in the present work is the transformation of N-bromoacetanilide into *p*-bromoacetanilide. As will be shown later, this reaction takes place without complications, and shows general acid catalysis in a variety of solvents. The transformation of the analogous compound N-chloroacetanilide to *p*-chloroacetanilide has been the subject of much investigation in aqueous solution. The reaction is not, however, one of simple acid catalysis, since the halogen acids have a specific effect, other acids having practically no catalytic power.†

It may be mentioned here that N-chloroacetanilide was found to be unaffected by standing at room temperature for a week in a 0·1 N solution of trichloracetic acid in benzene. (N-bromoacetanilide under the same conditions is one-half transformed in about 12 hours.)

Experimental Method.

N-bromoacetanilide was prepared as described by Slosson,‡ by the action of hypobromous acid upon acetanilide. The crystals which separated out were washed with a little ice water and dried in a vacuum desiccator in a dish protected from the light. The purity of the product (as determined by titrating the iodine liberated from potassium iodide) was 92–97%. Since the *p*-bromoacetanilide obtained by heating the above product melted at 165° without further purification, the chief impurity present in the N-bromoacetanilide was certainly *p*-bromoacetanilide. The appearance of the original product under the microscope serves as a convenient index of its purity, since it is easy to detect the needles of *p*-bromoacetanilide among the flat plates of N-bromoacetanilide.

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* 'J. Amer. Chem. Soc.,' vol. 53, p. 2478 (1931).

† See Rivett, 'Z. phys. Chem.,' vol. 85, p. 113 (1913). *Cf.* also the investigations in acetic acid and alcohol solutions by Blanksma, 'Rec. Trav. chim.,' vol. 21, p. 367 (1902), vol. 22, p. 290 (1903), and Fontein, *ibid.*, vol. 47, p. 635 (1928).

‡ 'Ber. deuts. chem. Ges.,' vol. 28, p. 3266 (1894).

It was found that the solid could be kept unchanged indefinitely over phosphorus pentoxide in the dark, but that the slightest trace of moisture initiated the change to *p*-bromoacetanilide, which then proceeded rapidly to completion.

The method used in determining the reaction velocity depends on the reaction of N-bromoacetanilide with acid potassium iodide solution,

$$C_6H_5NBrCOCH_3 + 2I^- + H^+ \rightarrow C_6H_5NHCOCH_3 + I_2 + Br^-.$$

The liberated iodine is titrated with sodium thiosulphate. The reaction takes place instantaneously and completely at ordinary temperatures, and *p*-bromoacetanilide has no action upon potassium iodide.

The reactions took place in glass-stoppered flasks of 50 c.c. capacity, which were enamelled black externally. The solutions studied were always about 0·01 N with respect to N-bromoacetanilide, and 2 c.c. samples were titrated at intervals. Although the colour of the starch used as indicator was somewhat modified by the organic solvent, it was found possible with practice to obtain titres reproducible to ± 0·1 c.c., provided that the concentrations of starch and potassium iodide were kept approximately constant. In order to find the absolute titration error involved (owing to the fact that a finite iodine concentration is necessary to produce a visible blue colour) some check titrations were carried out using a differential electrometric method. It was found that under the conditions used in the kinetic measurements, the blue colour invariably disappeared 0·2–0·4 c.c. before the true end-point. Since the titres obtained in an actual measurement of reaction velocity usually ranged between 7 c.c. and 20 c.c. a constant error of this magnitude will have very little effect on either the constancy or the absolute values of the monomolecular velocity constants calculated from these titres. The time-consuming method of electrometric titration was therefore only employed in the experiments with picric acid, where the bright yellow colour of the solutions made the use of starch impossible.

It is obviously of importance that none of the materials used should either liberate iodine from potassium iodide or react with iodine. This restriction made it impossible to work with a number of solvents, *e.g.*, paraldehyde, symm. tetrachloroethane, di-ethyl ether, and di-isoamyl ether were all found to exhibit oxidizing properties, even after drastic purification. Of the acid catalysts used α . β . dibromopropionic acid is known to liberate iodine from potassium iodide,* but it was found that by working at 0° this reaction is slow enough to enable rapid titrations to be carried out. Other reactions which might be expected to interfere with the titration—the reaction of monochloroacetic acid with potassium iodide† and the reaction of phenylpropiolic acid with iodine‡—were found to be negligible under the conditions of titration. All the materials used in the kinetic measurements were tested for oxidizing properties and reaction with iodine.

Catalysis in Chlorobenzene Solution.

N-bromoacetanilide was found to be completely stable in the following solvents: benzene, toluene, chlorobenzene, bromobenzene, carbon tetrachloride, and tetrachloroethylene. With the exception of tetrachloroethylene (which was prepared by fractionating a commercial product) these solvents were pure products which were dried over anhydrous potassium carbonate and redistilled. Solutions of N-bromoacetanilide 0·01 N by volume were made up in each of these solvents, and were kept in the dark in glass-stoppered bottles, no special precautions being taken to exclude moisture. No change of titre was observed for solutions in toluene, bromobenzene, carbon tetrachloride, and tetrachloroethylene after standing for a month, while solutions in benzene and chlorobenzene were kept for 1½ and 2½ years respectively without undergoing any change.

The addition of acids to any of the above solutions causes the transformation to *p*-bromoacetanilide to take place at a measurable speed. The majority of the experiments were carried out in chlorobenzene, since it is the solvent of the highest dielectric constant in which N-bromoacetanilide is completely stable, and thus might be expected to possess the smallest associating power. Measurements in other solvents will be described in the next section. The reactions were followed until about two-thirds of the N-bromoacetanilide had disappeared, and were always found to be monomolecular. The *p*-bromoacetanilide formed thus has no effect upon the course of the reaction, and the presence of this substance in the original N-bromoacetanilide is therefore unobjectionable. Table I gives a typical set of titration values.

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* Biilman, 'Rec. Trav. Chim.,' vol. 36, p. 319 (1917).

† Abderhalden and Guggenheim,' Ber. deuts. chem. Ges.,' vol. 41, p. 2853 (1933).

‡ James and Sudborough, 'Trans. Chem. Soc.,' vol. 91, p. 1042 (1907); Moelwyn-Hughes and Legard, *ibid.*, p. 424 (1933).

Table I.—*0·0260 N-trichloracetic Acid in Chlorobenzene at 15°.*

Time (hours).	Titre (c.c.).	100 k_{15}.
0	14·50	—
2·0	13·90	0·90
4·0	13·15	1·05
7·5	12·00	1·08
10·5	11·05	1·13
20·0	8·70	1·10
23·0	8·20	0·99
31·5	6·75	1·00
34·0	6·45	1·03
45·0	5·05	1·02
48·0	4·65	0·99
	Mean	1·03

The velocity constants in this and all subsequent tables correspond to the equation

$$kt = \log_{10}\frac{a}{x},$$

where t is the time in hours, a the initial titre, and x the titre after time t. The constants in the following tables were obtained by plotting $\log_{10} x$ against t and measuring the slope of the straight line obtained, thus eliminating any systematic error due to an error in the initial titre.

If acid was added to a more concentrated solution of N-bromoacetanilide in chlorobenzene, white needles separated out after standing for a few days. After washing with benzene and drying in air these needles melted sharply at 165° (Beilstein gives 165·5° for *p*-bromoacetanilide). This observation, together with the fact that the reaction is strictly monomolecular with acid concentrations as low as 0·003 N (see Table II), constitutes good evidence that the change measured is the simple catalysed transformation into *p*-bromoacetanilide.

Most of the catalysts employed were carboxylic acids. It would be of interest to obtain data for a larger number of phenol derivatives, but the majority of phenols are brominated rapidly by N-bromoacetanilide, *e.g.*,

$$C_6H_5OH + C_6H_5NBrCOCH_3 \rightarrow p\text{-}BrC_6H_4OH + C_6H_5NHCOCH_3.$$

Of the phenols actually studied, pentachlorophenol obviously cannot be brominated, and picric acid and 2 . 4 . 6 . trichlorophenol do not react with free bromine at ordinary temperatures. The range of concentrations studied varied with the acid used. Its lower limit was determined by the point at which the reaction became too slow to be measured conveniently, the slowest reactions studied having a half time of about 20 days. In an upward direction the range was often limited by the solubility of the acid, but was otherwise carried up to about 0·3 N.

Materials.

Trichloracetic acid, *α-bromopropionic acid*, and *trichlorophenol* were pure products, dried in a vacuum desiccator. Pure *dichloracetic acid* was distilled, the portion boiling at 191–192·5° being used. It contained no free hydrochloric acid. *Monochloracetic acid* was recrystallized from pure benzene. α . β-*dibromopropionic acid* was recrystallized from ligroin and dried *in vacuo*. A preparation of β-*chloropropionic acid* of unknown origin was dried *in vacuo*. Titration indicated a purity of 99·6%. *Cinnamic acid* was recrystallized from water and dried *in vacuo*. *Picric acid* was recrystallized from carbon tetrachloride.

β-*Phenylpropiolic acid* was prepared from ethyl cinnamate by bromination in ether and hydrolysis of the resulting ethyl β-phenyl-α . β-dibromopropionate with alcoholic potash. The acid was liberated by adding dilute sulphuric acid and recrystallized from water. Melting point 135°.

Phenoxyacetic acid was prepared from phenol and monochloracetic acid as described by Giacosa.[*] It was recrystallized from water and melted at 97°.

Acetic acid.—A pure preparation was frozen, and three-quarters allowed to melt and poured off. This process was repeated three times, and the resulting product melted at 15·8°.

Pentachlorophenol was prepared from hexachlorobenzene by the action of sodium hydroxide and glycerol, as described by Weber and Wolff.[†] It was recrystallized from benzene and melted at 187°.

Results in Chlorobenzene.

In the following tables,

c = acid concentration in volume normality.

k_{15}, k_{25} = monomolecular velocity constants at 15° and 25° respectively.

$\alpha = k_{15}/c$.

α_0 = value of α at infinite dilution. The method of extrapolating will be described in the next section.

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[*] 'J. Prakt. Chem.,' vol. 19, p. 396 (1879).

[†] 'Ber. deuts. chem. Ges.,' vol. 18, p. 335 (1885).

Table II.—Trichloracetic Acid in Chlorobenzene.

c	100 k_{15}.	100 k_{25}.	k_{25}/k_{15}.	10α.
0·00359	0·139	—	—	3·87
0·00520	0·203	—	—	3·90
0·00780	0·324	0·629	1·94	4·14
0·0130	0·552	—	—	4·25
0·0156	0·588	1·17	1·99	3·75
0·0182	0·744	—	—	4·09
0·0235	0·820	1·65	2·00	3·50
0·0260	1·04	—	—	4·00
0·0325	1·18	—	—	3·63
0·0390	1·40	—	—	3·58
0·0520	1·78	—	—	3·42
0·0780	2·54	—	—	3·08
0·104	3·04	—	—	2·92
0·130	3·62	—	—	2·78
0·182	4·75	—	—	2·61
0·260	5·92	—	—	2·28
		Mean …………	1·98	$\alpha_0 = 4\cdot1 \times 10^{-1}$

Table III.—Dichloracetic Acid in Chlorobenzene.

c.	10^3 k_{15}.	10^3 k_{25}.	k_{25}/k_{15}.	100α.
0·0144	2·23	4·91	2·20	15·5
0·0240	3·15	6·90	2·19	13·1
0·0325	3·60	8·02	2·23	11·0
0·0353	4·72	—	—	13·4
0·0480	5·31	—	—	11·1
0·0719	6·90	—	—	9·61
0·120	8·22	—	—	6·86
0·168	11·2	—	—	6·67
		Mean …………	2·21	$\alpha_0 = 17 \times 10^{-2}$

Table IV.—Phenylpropiolic Acid in Chlorobenzene.

c.	10^3 k_{15}.	10^3 k_{25}.	k_{25}/k_{15}.	100α.
0·0250	1·78	4·06	2·28	7·10
0·0350	2·30	5·21	2·27	6·60
0·0500	3·00	6·69	2·23	6·00
0·100	3·58	—	—	3·58
		Mean …………	2·26	$\alpha_0 = 8\cdot3 \times 10^{-2}$

Table V.—Monochloracetic Acid in Chlorobenzene.

c.	$10^3 k_{15}$.	$10^3 k_{25}$.	k_{25}/k_{15}.	$100a$.
0·0325	1·94	4·49	2·30	5·96
0·0433	2·72	—	—	6·28
0·0485	2·60	6·44	2·47	5·35
0·0649	3·61	8·18	2·25	5·59
0·0649	3·21	—	—	4·80
0·0649	3·27	—	—	5·05
0·0974	4·38	10·50	2·39	4·96
0·108	5·03	—	—	4·67
0·172	7·04	—	—	4·10
0·216	8·12	—	..	3·75
		Mean	2·35	$a_0 = 6·7 \times 10^{-2}$

Table VI.—Phenoxyacetic Acid in Chlorobenzene.

c.	$10^3 k_{15}$.	$10^3 k_{25}$.	k_{25}/k_{15}.	$100a$.
0·0128	0·633	1·63	2·41	4·96
0·0213	1·06	2·55	2·40	4·95
0·0340	1·46	3·33	2·28	4·27
0·0425	1·52	3·68	2·42	3·58
0·0635	1·98	4·65	2·35	3·11
0·0745	2·28	5·58	2·44	3·06
0·0754	2·44	5·65	2·32	3·05
		Mean	2·41	$a_0 = 5·7 \times 10^{-2}$

Table VII.—β-Chloropropionic Acid in Chlorobenzene.

c.	$10^3 k_{15}$.	$100a$.
0·0660	1·22	1·85
0·110	1·90	1·73
0·220	3·24	1·47
		$a_0 = 2·1 \times 10^{-2}$

Table VIII.—Acetic Acid in Chlorobenzene.

c.	$10^3 k_{15}$.	$100a$.
0·0573	0·87	1·62
0·096	1·49	1·54
0·191	2·04	1·06
0·288	3·24	1·12
		$a_0 = 1·7 \times 10^{-2}$

Table IX.—Cinnamic Acid in Chlorobenzene.

c.	$10^4 k_{15}$.	100α.
0·0310	5·11	1·65
0·0405	6·35	1·57
0·0570	8·55	1·50
0·0810	11·7	1·45
		$\alpha_0 = 1 \cdot 8 \times 10^{-2}$

Table X.—2 . 4 . 6 . Trichlorophenol in Chlorobenzene.

c.	$10^3 k_{15}$.	$10^3\alpha$.
0·125	0·538	4·3
0·250	1·00	4·0
0·500	2·20	4·4
	Mean	$4 \cdot 2 \times 10^{-3}$

Table XI.—Pentachlorophenol in Chlorobenzene.

c.	$10^3 k_{15}$.	100α.
0·0800	1·05	1·31
0·120	1·29	1·08
0·160	2·00	1·25
0·200	2·56	1·28
	Mean	$1 \cdot 2 \times 10^{-2}$

Table XII.—Picric Acid in Chlorobenzene.

c.	$10^3 k_{15}$.	100α.
0·085	1·0	1·2
0·152	1·9	1·2
	Mean	$1 \cdot 2 \times 10^{-2}$

It will be seen from Tables II–XII that α, the catalytic constant of the acid, in general decreases with increasing concentration. Fig. 1 illustrates this for trichloracetic acid (*cf.* Table II), and also serves to show the degree of reproducibility of the results. Several different samples of N-bromoacetanilide, chlorobenzene, and trichloracetic acid were used, and the interval between the first and last experiments was over two years.

The variation of catalytic power with concentration may be caused by an actual association of the carboxylic acid molecules to form definite double molecules, or it may be due to a medium effect (possibly conditioned largely by the presence of dipoles in the acid molecules) analogous to the salt effects which are well known in aqueous solutions.*

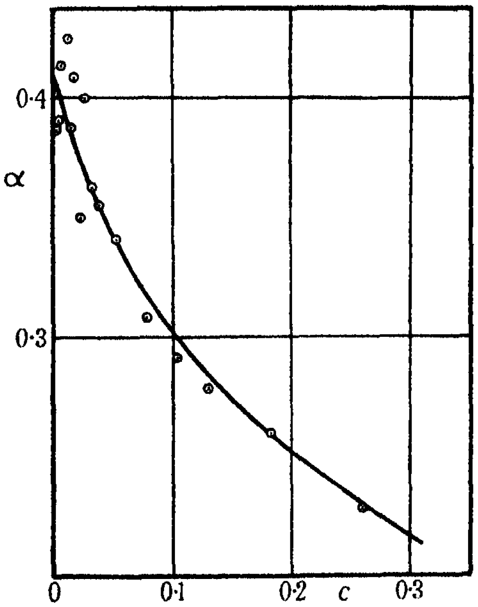

Fig. 1.

The point will not be discussed here; we should, however, expect that the plot of α against c will become linear at low concentrations,† and it is upon this principle that the extrapolations to infinite dilution have been made. Fig. 1

---

* *Cf.* Brönsted and Bell, *loc. cit.*

† This is clearly so for any type of medium effect not involving ions. For a chemical association, let α_0 and β_0 be the catalytic constants for the single (A) and double (A_2) molecules respectively; then the velocity constant is given by

$$k = \alpha_0[A] + \beta_0[A_2].$$

For the equilibrium between A and A_2, $[A_2] = K[A]^2$, and since at low concentrations practically all the acid will be present as single molecules,

$$[A] = c - [A_2], \qquad [A_2] \sim Kc^2,$$

$$k \sim \alpha_0(c - Kc^2) + \beta_0 Kc^2, \qquad \alpha = \frac{k}{c} \sim \alpha_0 - (\alpha_0 - \beta_0)Kc.$$

shows that this method of extrapolation is valid for trichloracetic, acid, and fig. 2 shows the corresponding curves for dichloracetic, monochloracetic, and phenoxyacetic acids. The most doubtful extrapolation carried out is that for dichloracetic acid ; however, by analogy with the other acids there can hardly be an error of more than 10% in the value of α_0 obtained. The somewhat meagre data for the phenolic acids, Tables X, XI, and XII, show no regular variation of catalytic power with concentration. This makes it probable that the variation in α observed for the carboxylic acids is due to an actual stochiometric association, since although the phenols and alcohols are often termed associated on account of their deviations from the laws of dilute solution, there is no evidence for the formation of definite molecular aggregates.*

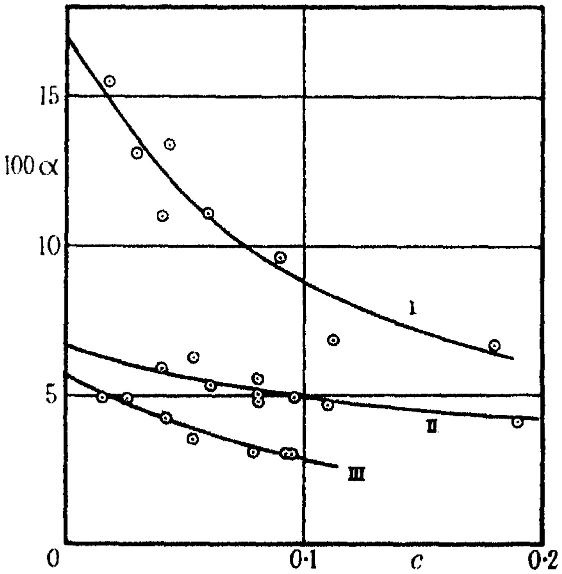

Fig. 2.—I, Dichloracetic acid ; II, monochloracetic acid ; III, phenoxyacetic acid.

The Relation between Acidic Strength and Catalytic Power.

Since no measurements of acid-base equilibria have been carried out in chlorobenzene, dissociation constants in water constitute our only quantitative measure of the relative strengths of the acids employed. Table XIII shows the dissociation constants and values of α_0 for the acids investigated.

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* *Cf.* Meisenheimer and Dauer, 'Liebigs Ann.,' vol. 482, p. 130 (1930).

Unless otherwise stated, the values for the dissociation constants are taken from Landolt-Börnstein Tables. The values for the chlorophenols are taken from the work of Tiessens.*

Trichloracetic acid is too strong an acid for its dissociation constant in water to be measured directly. It has, however, been found† for a number of carboxylic acids that the ratio between the dissociation constants in water and ethyl alcohol is approximately constant and equal to $6 \cdot 4 \times 10^5$. The value 0·8 given above for K_d was therefore obtained by multiplying the value $1 \cdot 25 \times 10^{-6}$ obtained by Goldschmidt in ethyl alcohol by the factor $6 \cdot 4 \times 10^5$.

Table XIII.

Acid.	K_d.	α_0 (observed).	α_0 (calculated).
2 . 4 . 6 . trichlorophenol	$3 \cdot 9 \times 10^{-7}$	0·0042	0·0050
Pentachlorophenol	$5 \cdot 5 \times 10^{-6}$	0·012	0·012
Acetic	$1 \cdot 8 \times 10^{-5}$	0·017	0·017
Cinnamic	$3 \cdot 7 \times 10^{-5}$	0·021	0·021
β-chloropropionic	$8 \cdot 6 \times 10^{-5}$	0·026	0·026
Phenoxyacetic	$7 \cdot 6 \times 10^{-4}$	0·053	0·053
Monochloracetic	$1 \cdot 6 \times 10^{-3}$	0·063	0·063
Phenylpropiolic	$5 \cdot 9 \times 10^{-3}$	0·091	0·091
Dichloracetic	$5 \cdot 0 \times 10^{-2}$	0·17	0·17
Trichloracetic	$8 \cdot 0 \times 10^{-1}$	0·41	0·43

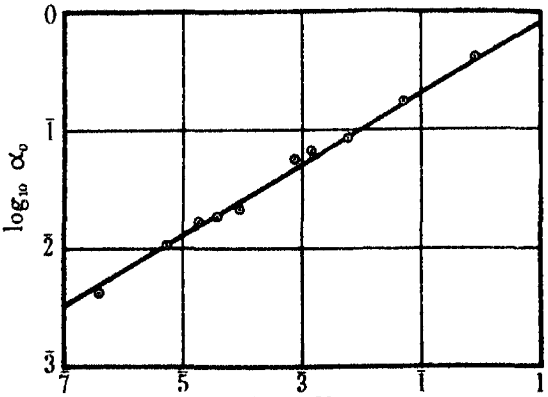

FIG. 3.

It is immediately obvious from Table XIII that the catalytic power increases in the same order as the dissociation constants, but much more slowly. Fig. 3 shows $\log_{10} \alpha_0$ plotted against $\log_{10} K_d$; the points fall well on a straight line.

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* 'Rec. trav. chim.,' vol. 48, p. 1066 (1929).

† See, *e.g.*, Larsson, 'Diss. Lund,' (1924); Goldschmidt, 'Z. phys. Chem.,' vol. 99, p. 116 (1921); Bright and Briscoe, 'J. Phys. Chem.,' vol. 37, p. 787 (1933).

The fourth column of Table XIII contains the values of α_0 calculated from the equation

$$\alpha_0 = 0{\cdot}45\ K_d^{0{\cdot}30}. \tag{3}$$

There is good agreement between the calculated and observed values.

These results indicate a quantitative relation between the relative tendencies for an acid to lose a proton in the two solvents water and chlorobenzene. Similar conclusions have been reached by the study of acid base equilibria in different solvents. Thus, as mentioned above, there is an approximately constant ratio between the dissociation constants of an uncharged acid in water and ethyl alcohol.

In an aprotic solvent such as chlorobenzene (*i.e.*, a solvent which possesses neither acidic nor basic properties), there is no " dissociation constant " for an acid unless a third basic substance is added. This basic substance may be an indicator, when measurements of the equilibrium constant of the reaction

$$HA + B \rightleftarrows (A)^- \ (BH)^+$$

can readily be carried out. No measurements of this kind have been carried out in chlorobenzene, but the results of Brönsted* and La Mer and Downes† for benzene solutions, and of Hantzsch and Voigt‡ for chloroform solutions indicate that the order of strength of neutral acids in these solvents is nearly the same as it is in water.

Wynne-Jones§ has recently suggested on theoretical and experimental grounds that the relative strengths of acids of the same electrical type do not remain unchanged on passing from one solvent to another, but change in a regular way depending on the dielectric constant of the solvent and the radius of the ions. If the effects indicated by Wynne-Jones for water and the alcohols are real, extrapolation on his theory to media of very low dielectric constant would lead to relative strengths differing very much from those in water. This conclusion is not supported by the catalytic measurements described here or the indicator measurements quoted in the preceding paragraph.

Picric acid (see Table XII) was found to have a catalytic constant at least 15 times smaller than that predicted by equation (3). This cannot be due to the change from carboxylic to phenolic acid, since the chlorophenols agree well with equation (3). The decrease in dissociation constant in passing from water to ethyl alcohol is very much less for picric acid and *p*-nitrophenol than for the carboxylic acids.* (No other phenols have been studied.) If, however, we follow Wynne-Jones' extrapolation of this effect to solvents of low dielectric constant, picric acid should be about 10^{10} times as strong as trichloracetic acid in chlorobenzene, while actually its catalytic power is 30 times smaller.†

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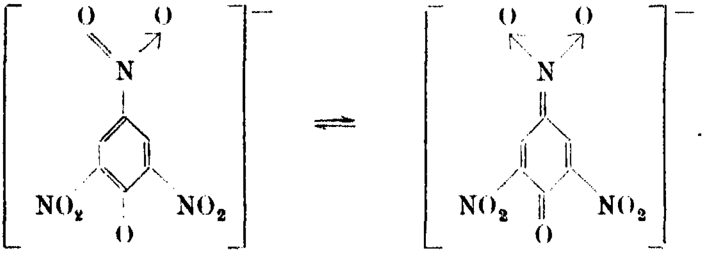
* ' Ber. deuts. chem. Ges.,' B, vol. 61, p. 2049 (1928).

† ' J. Amer. Chem. Soc.,' vol. 55, p. 1840 (1933).

‡ ' Ber. deuts. chem. Ges.,' B, vol. 62, p. 975 (1929).

§ ' Proc. Roy. Soc.,' A, vol. 140, p. 440 (1933).

The abnormal behaviour of picric acid as regards dissociation constant and catalytic power is probably attributable to the possibility of tautomerism in the picrate ion, *i.e.*,



The equilibrium between these two forms may vary very much with the solvent, and hence the dissociation constant (which involves the total concentration of both forms of the ion) may behave irregularly. Further, Brönsted‡ has pointed out that in such pseudo-acid equilibria the dissociation constant no longer gives a true measure of the tendency of the acid molecule to lose a proton. The same type of equilibrium can occur with *p*-nitrophenol, but not with the chlorophenols. It would be of interest to measure the dissociation constants of the latter compounds in the alcohols.

The Molecular Statistics of Catalysis in Chlorobenzene.

From a kinetic standpoint the catalysis studied here is equivalent to a bimolecular reaction between the acid and N-bromoacetanilide. If the catalytic constants (in the appropriate units) are expressed in the form

$$\alpha_0 = Be^{-A/RT} \tag{4}$$

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* See, *e.g.*, Larsson (*loc. cit.*).

† It may also be noted that in the acidity series in benzene obtained by Brönsted (' Ber. deuts. chem. Ges.,' B, vol. 61, p. 2049 (1928)), picric acid falls between monochloracetic and dichloracetic acids, *i.e.*, it is relatively somewhat *weaker* than in water.

‡ Brönsted and Pedersen, ' Z. phys. Chem.,' vol. 108, p. 185 (1924) ; *cf.* also Pedersen (*loc. cit.*).

*it becomes of interest to discover whether B in equation (4) can be identified with the collision number.**

A knowledge of the temperature coefficient is necessary to express the observed reaction velocity in the form of equation (4). Measurements were only carried out for the five strongest acids, since it is necessary to use only dilute solutions, where the part played by association is small. It will be seen from Tables II–VI that the temperature coefficient does not vary systematically with the concentration over the range studied. Table XIV contains the mean values of k_{25}/k_{15} and the calculated values of A and B. A is expressed in calories per gram molecule and B in gram molecules per litre per second.

Table XIV.

Acid.	k_{25}/k_{15}.	A.	$\log_{10}$ B.
Phenoxyacetic	2·41	15,000	6·9
Monochloracetic	2·35	14,600	6·6
Phenylpropiolic	2·26	13,900	6·3
Dichloracetic	2·21	13,800	6·5
Trichloracetic	1·90	11,800	5·4

If B represents a collision number, it should be of the order of magnitude 10^{10}–10^{11} in the units employed. The observed values are 10^4–10^5 times smaller than this, *i.e.*, of the collisions which occur with sufficient energy, only one in 10^4–10^5 results in reaction. Some factor other than the energy of activation must thus be of importance.

Catalysis in other Solvents.

It is obviously of interest to obtain data for the same reaction in a number of solvents. Unfortunately, none of the other solvents investigated proved so suitable as chlorobenzene.

A large number of experiments was carried out in *benzene*. The benzene was a highly purified product, dried over P_2O_5 and distilled. The determinations were carried out exactly as for the chlorobenzene solutions, and all the reactions were strictly monomolecular. The results given in Tables XV–XX were obtained.

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* See Moelwyn-Hughes, 'Chem. Rev.,' vol. 10, p. 241 (1932); 'Phil. Mag.,' vol. 14, p. 112 (1932).

Table XV.—Trichloracetic Acid in Benzene.

c.	$100\ k_{15}$.	$10a$.
0·00944	0·197	2·08
0·0158	0·299	1·89
0·0315	0·544	1·76
0·0472	0·833	1·88
0·0620	1·14	1·81
0·0785	1·48	1·89
0·110	2·02	1·83
0·157	3·04	1·93
0·236	4·28	1·81
0·315	5·61	1·79
	Mean	$1·87 \times 10^{-1}$

Table XVI.—Dichloracetic Acid in Benzene.

c.	$10^3\ k_{15}$.	$100a$.
0·0282	1·77	6·28
0·0323	2·08	6·43
0·0560	2·74	4·88
0·0783	4·11	5·23
0·113	5·24	4·66
0·169	7·72	4·47
0·169	7·92	4·70
0·203	10·2	5·02
0·247	9·60	3·89
0·291	12·8	4·38
	Mean	$5·00 \times 10^{-2}$

Table XVII.—α . β-Dibromopropionic Acid in Benzene.

c.	$10^3\ k_{15}$.	$100a$.
0·0273	1·27	4·65
0·0456	1·96	4·30
0·0638	2·71	4·26
0·0902	3·52	3·80
0·130	4·13	3·17
0·200	5·02	2·51
	Mean	$3·78 \times 10^{-2}$

Table XVIII.—Monochloracetic Acid in Benzene.

c.	$10^3 k_{15}$.	100α.
0·0378	1·12	2·96
0·0397	1·06	2·66
0·0596	1·41	2·36
0·0756	1·66	2·13
0·0795	1·63	2·05
0·110	2·20	2·00
0·139	2·59	1·86
0·199	3·27	1·74
0·284	4·23	1·49
0·298	4·15	1·38
0·397	4·97	1·25
0·497	5·98	1·20
	Mean	$1·92 \times 10^{-2}$

Table XIX.—α-Bromopropionic Acid in Benzene.

c.	$10^3 k_{15}$.	100α.
0·0650	2·43	3·74
0·130	3·19	2·45
0·148	3·26	2·20
0·206	4·18	2·02
0·235	4·33	1·84
0·295	5·10	1·73
0·383	6·54	1·70
	Mean	$2·24 \times 10^{-2}$

Table XX.—β-Chloropropionic Acid in Benzene.

c.	$10^3 k_{15}$.	$10^3\alpha$.
0·0900	0·890	9·9
0·135	1·15	8·5
0·224	2·33	10·2
	Mean	$9·5 \times 10^{-3}$

An examination of the data in Tables XV–XX shows that it is impossible to carry out any consistent extrapolation of the catalytic constants to infinite dilution. Thus while the results for α . β-dibromopropionic acid can be extrapolated just as in chlorobenzene, the catalytic constant of trichloracetic acid remains constant over the whole concentration range, and those of dichloracetic and α-bromopropionic acids are practically constant at high concentrations, but increase rapidly in dilute solutions. This is probably due to the fact that carboxylic acids in benzene are almost entirely present as double molecules at the concentrations studied.* The smaller tendency to association in chlorobenzene is in harmony with its higher dielectric constant.

Since no comparable values of α_0 can be obtained by extrapolation, we have sought to obtain a semi-quantitative idea of the relative catalytic powers of the acids by taking the mean value of α in each case. Since the concentration ranges studied are similar for the different acids, these mean values should be roughly comparable. Table XXI contains the mean catalytic constants α_m and the values of K_d the dissociation constant in water. Fig. 4 shows $\log_{10} \alpha_m$ plotted against $\log_{10} K_d$.

Table XXI.

Acid.	K_d.	α_m.
β-Chloropropionic	$8 \cdot 6 \times 10^{-5}$	0·0095
α-Bromopropionic	$1 \cdot 1 \times 10^{-3}$	0·022
Monochloracetic	$1 \cdot 6 \times 10^{-3}$	0·019
α . β-Dibromopropionic	$6 \cdot 3 \times 10^{-3}$	0·038
Dichloracetic	$5 \cdot 0 \times 10^{-2}$	0·050
Trichloracetic	$8 \cdot 0 \times 10^{-1}$	0·19

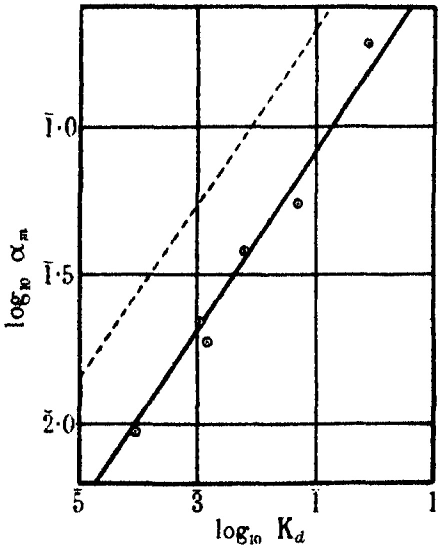

Fig. 4.

The points in fig. 4 lie fairly well upon a straight line. The dotted line in the figure is the line previously obtained for chlorobenzene solutions. The two straight lines are parallel, the catalytic constants in benzene each being about three times smaller than in chlorobenzene. The catalysis appears to follow very similar laws in the two solvents, and the difference found in the absolute values of the catalytic constants is at least in part due to association, the values in chlorobenzene being extrapolated to infinite dilution, while those in benzene are mean values for a finite concentration range.

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* See, *e.g.*, Tollens, 'Ber. deuts. chem. Ges.,' vol. 48, p. 489 (1915); Rabinowitsch 'Z. phys. Chem.,' vol. 132, p. 83 (1928).

It is probable that the same difficulties of extrapolation would be met with in carbon tetrachloride, toluene, and tetrachloroethylene, the other solvents in which N-bromoacetanilide was found to be completely stable in absence of acid. These difficulties could be avoided by using a solvent of much higher dielectric constant in which association is negligible; unfortunately, however, N-bromoacetanilide reacts rapidly with all alcohols, ketones, and esters, so that these types of solvent could not be used.

It was, however, found possible to carry out approximate measurements of catalysis in *ethylene chloride* (D.C. = 10) and *ethyl nitrate* (D.C. = 14), which were obtained by drying Kahlbaum products with anhydrous potassium carbonate and fractionating. Even in these solvents N-bromoacetanilide disappears slowly in the absence of acid, probably owing to some oxidation reaction. This spontaneous reaction is being studied further; for the present it is sufficient to state that the initial stages are not reproducible, but that the reaction always proceeds only to a very small extent during the first 10·20 hours. It was therefore possible to carry out measurements of acid catalysis provided that the catalysed reaction was sufficiently fast. For values of k_{15} greater than about 0·01 the reaction was followed for 12 hours (or less) and the monomolecular constant determined in the usual way. For slower reactions, the measurements were extended over longer periods, and the initial velocity of the catalysed reaction obtained graphically. The results in Tables XXII–XXV are therefore only approximate, particularly for the slower reactions.

Table XXII.—Trichloracetic Acid in Ethyl Nitrate and Ethylene Chloride.

Ethyl nitrate.			Ethylene chloride.		
c.	100 k_{15}.	10a.	c.	10 k_{15}.	10a.
0·0490	1·59	3·24	0·0447	0·442	9·9
0·0980	2·94	3·00	0·0744	0·810	10·8
0·152	4·02	2·65	0·0970	1·02	10·5
0·196	5·45	2·78	0·149	1·90	12·8
			0·194	2·40	12·4
	Mean	$2·92 \times 10^{-1}$		Mean	$11·3 \times 10^{-1}$

Table XXIII.—Dichloracetic Acid in Ethyl Nitrate and Ethylene Chloride.

Ethyl nitrate.			Ethylene chloride.		
c.	100 k_{15}.	10α.	c.	100 k_{15}.	10α.
0·0822	1·18	1·43	0·070	0·86	1·23
0·123	1·90	1·54	0·123	1·23	1·00
0·150	2·05	1·36	0·175	2·08	1·19
0·210	2·34	1·11	0·263	2·22	0·86
	Mean	$1{\cdot}38 \times 10^{-1}$		Mean	$1{\cdot}07 \times 10^{-1}$

Table XXIV.—Phenylpropiolic Acid in Ethyl Nitrate and Ethylene Chloride.

Ethyl nitrate.			Ethylene chloride.		
c.	10^3 k_{15}.	100α.	c.	100 k_{15}.	100α.
0·100	5·2	5·2	0·0935	1·07	12·4
0·150	9·3	6·2	0·133	1·24	9·3
0·200	15·2	7·6	0·200	1·62	8·1
			0·200	1·76	8·8
	Mean	$6{\cdot}3 \times 10^{-2}$		Mean	$9{\cdot}6 \times 10^{-2}$

Table XXV.—Monochloracetic Acid in Ethylene Chloride.

c.	10^3 k_{15}.	100α.
0·100	4·7	4·7
0·100	3·9	3·9
0·200	6·6	3·3
0·200	4·0	2·0
0·300	6·9	2·3
	Mean	$3{\cdot}2 \times 10^{-2}$

It is seen that the values of the catalytic constants exhibit no regular change with concentration, so that the mean values can safely be taken. The order of catalytic power is again the same as that of the dissociation constants in water, but the results are not sufficiently accurate to draw any more quantitative conclusions. Table XXVI contains the catalytic constants for four acids in the four solvents so far mentioned.

Table XXVI.—Catalytic Constants.

	Chlorobenzene.	Benzene.	Ethyl nitrate.	Ethylene chloride.
Trichloracetic	0·41	0·19	0·29	1·13
Dichloracetic	0·17	0·050	0·14	0·11
Phenylpropiolic	0·091	—	0·063	0·096
Monochloracetic	0·063	0·019	—	0·032

Changing from one solvent to another thus produces at the most a threefold change in the catalytic power of a given acid.

In order to test further the effect of the medium upon catalysis, experiments were carried out with trichloracetic acid in bromobenzene, carbon tetrachloride, tetrachloroethylene, and chloroform. N-bromoacetanilide is completely stable in the first three solvents, and in chloroform the spontaneous change is too slow to affect the results. All the reactions were strictly monomolecular. Two experiments were carried out in each solvent, using approximately 0·1 and 0·2 N-trichloracetic acid. The results, together with data for the solvents previously dealt with, are given in Table XXVII.

Table XXVII.—Trichloracetic Acid in various Solvents.

Solvent.	0·1 N.			0·2 N.		
	c.	100 k_{18}.	$10a$.	c.	100 k_{18}.	$10a$.
Benzene	0·110	2·02	1·83	0·236	4·28	1·81
Chlorobenzene	0·104	3·04	2·92	0·182	4·75	2·61
Bromobenzene	0·102	2·82	2·76	0·205	5·44	2·65
Carbon tetrachloride	0·088	3·72	4·25	0·175	6·44	3·68
Tetrachloroethylene	0·108	6·85	6·32	0·215	10·7	4·98
Chloroform	0·102	12·7	12·4	0·203	16·1	7·94
Ethylene chloride	0·097	10·2	10·5	0·194	24·0	12·4
Ethyl nitrate	0·098	2·94	3·00	0·196	5·45	2·78

The variations in the catalytic power of trichloracetic acid are all within a power of 10. These variations may again be partly due to differences in degree of association in the different solvents.

In conclusion, the author wishes to express his thanks to Professor J. N. Brönsted for his advice and assistance throughout this work.

Summary.

(1) The monomolecular transformation of N-bromoacetanilide to *p*-bromoacetanilide is catalysed by acids in a number of solvents.

(2) The catalytic constants of ten acids in chlorobenzene bear a simple relationship to their dissociation constants in water. Picric acid is an exception to this relation.

(3) Results in benzene, though less accurate, indicate that a similar relationship holds in this solvent. Experiments in six other solvents show that the medium has a comparatively small effect upon the catalytic constant.

(4) Measurements of the temperature coefficients for catalysis by five acids in chlorobenzene show that the velocity of reaction is 10^4–10^5 times smaller than the value calculated from the simple collision formula.

Corrosion and Co-ordination.

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(Communicated by H. T. Tizard, F.R.S.—Received August 2, 1933.)

According to Nernst's electrolytic solution tension theory, an incipient concentration of metal ions probably exists at the surface of metal immersed in water. If anions, which possess the property of combining with the metal ions to form undissociated molecules or complex ions, are present, then a mechanism whereby the metal passes into solution can readily be pictured. Assuming for convenience of notation that the metal M is divalent and the anion X monovalent, and that M and X form the sparingly dissociated complex anion $[M(X)_4]''$, then the processes which occur during the corrosion of the pure metal M, in an aqueous solution of the salt NaX can be described as follows.

A cation M is first removed from the surface of M as the undissociated complex ion $[M(X)_4]''$

$$M + 4X' + 4Na^{\cdot} = [M(X)_4]'' + 4Na^{\cdot} + 2\Theta.$$

The negative charge left on the metal immediately discharges 2 sodium ions and the sodium formed reacts with the water forming hydrogen and 2 molecules of sodium hydroxide. The liberation of gaseous hydrogen will depend upon the overvoltage of the metal. When this is high the corrosive process will be assisted by dissolved oxygen, which will oxidize the protective hydrogen film. For each atom of M passing into solution the equivalent quantity of hydroxyl, *i.e.*, 2OH, is formed, and therefore as the process proceeds, the alkalinity of the solution increases. Consequently sooner or later, according to the degree of dissociation of the complex ion formed, a point must be reached in a static system when further corrosion brings about the precipitation of either metal hydroxide or basic salt. It can be anticipated that in a system which precipitates a basic salt of the type $MX_2 . nM(OH)_2$, the total concentration of M in solution must pass through a maximum, for the production of 2OH in the corrosive process, once precipitation has begun, must bring about the precipitation of more than its equivalent quantity of M.

The complex ion formed must be in equilibrium with the simple salt

$$[M(X)_4]'' \rightleftharpoons MX_2 + 2X',$$

and therefore in systems where the simple salt is highly insoluble, its precipitation will occur as corrosion proceeds. This precipitation may be followed at a later stage in the process by the precipitation of a basic salt.

Consider a simple system in which a piece of pure metal is placed in an aqueous solution of NaX. Neglecting for the moment the effect of dissolved oxygen and assuming that the metal possesses only one valency and that disturbing factors such as film formation are absent, then it can be seen from the above theory that the initial velocity of the corrosive process must be governed by the following factors :—

(1) The electrolytic solution pressure of the metal.

The magnitude of this will govern the incipient concentration of ions on the surface of the metal.

(2) The tendency which the metal ions possess to form stable complex ions.

This tendency will depend upon the chemical nature of the metal and is a function of the electronic structure of the metal ion.*

(3) The co-ordinating tendency of the anion.

Little quantitative knowledge of the stability of complex ions in aqueous solution is available, but from general considerations of a qualitative nature and from measurements already carried out on the dissociation of certain copper-carboxylato complexes,* it appears certain that the co-ordinating tendency of an anion is governed largely by its polar properties.

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* Riley and Fisher, 'J. Chem. Soc.,' p. 2006 (1929); Riley and Ives, *ibid.*, p. 1998 (1931).

Certain facts are known which lend strong support to the above views, *e.g.*, copper (*a metal which forms a large number of stable complex salts*), in the presence of oxygen dissolves in ammonia (which possesses a high co-ordinating tendency), to form the complex compound $[Cu(NH_3)_4](NO_2)_2$.† Aluminium dissolves in dilute hydrochloric acid more readily than in dilute sulphuric acid of the same p_H, because the chloride ion has a greater co-ordinating tendency than the sulphate. A trace of nitrous acid catalyses the dissolution of copper in nitric acid; the nitrite ion forms complex ions which are more stable than those formed by the nitrate ion.

It was decided, in order to test the above theory, to measure the rate of solution of copper in aqueous solutions of the sodium salts of the following acids: oxalic, malonic, succinic, phthalic, carbonic, acetic, benzoic, citric, tartaric, and salicylic, and to compare the results obtained with those from a similar series of experiments employing nickel instead of copper. Both these metals are available in a high state of purity, which considerably simplifies the problem.

Experimental.

In order that a large number of independent experiments could be carried out, the procedure was made as simple as possible. 100 c.c. Pyrex conical flasks were employed in all experiments. Individual flasks differed from each other only slightly. 50 c.c. of a 0·2 N solution of the sodium salt under investigation were pipetted into the conical flask, a piece of thin sheet metal of standard size, 2 inches × 0·3 inches, bent once at right angles so that it would stand on its edge on the bottom of the flask, was added and the mouth of the flask covered loosely with a filter paper to exclude dust whilst allowing free access of air. The flask was set on one side in a room of fairly constant temperature (20° ± 2°). To compensate for evaporation, water was added from time to time up to a calibration on the side of the flask.

The standard pieces of electrolytic sheet copper and pure sheet nickel employed were washed, in ether, alcohol, and water to remove grease and then immersed in dilute nitric acid for a short time to remove any oxide film. The nitric acid was not sufficiently concentrated to produce effervescence or to dissolve any appreciable quantity of the metal itself. The standard pieces were then thoroughly washed with distilled water and alcohol and stored under alcohol, being dried thoroughly with filter paper before use. At least eight separate flasks were employed for each sodium salt. From time to time the liquid in one of the flasks was decanted from the metal, filtered where necessary, and the quantity of metal in solution determined by analysis. Ephraim's salicylaldoxime method was employed for copper and the dimethylglyoxime method for nickel. These methods possess the advantage that they can be carried out directly on the solutions without previous removal of the organic anions.

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* Riley and Ives, 'J. Chem. Soc.,' p. 2985 (1928); p. 1307 (1929); p. 1642 (1930).

† Bassett and Durrant, 'J. Chem. Soc.,' vol. 121, p. 2630 (1922).

Each point of the following curves represents a separate and independent experiment, the whole of the 50 c.c. of the sodium salt solution being used for each analysis.

Copper.

Sodium Oxalate.—The "A.R." salt was used. The results are shown in fig. 1. The bright copper became somewhat dulled after 3 or 4 days and a thin film of firmly adhering, brown tarnish covered the surface uniformly. This remained unchanged for about 60 days, the copper in the meantime dissolving at a relatively rapid and nearly uniform rate, to form a deep blue solution. On allowing some of this to evaporate, long sky-blue needles of $Na_2[Cu(C_2O_4)_2(H_2O)_2]$ separated. After 60 days the film on the copper darkened considerably and assumed a greenish sheen whilst a verdigris-like solid slowly separated on the copper and on the bottom of the flask. The precipitation, of what was probably basic copper oxalate (the amount was too small for purification and analysis), was accompanied by a pronounced decrease in the concentration of copper in solution.

Sodium Citrate.—The "A.R." salt was used and the results are shown in fig. 1. The copper remained bright throughout the run. The small but definite acceleration in the rate of solution of copper was probably due to two causes: (1) the increase in the surface area of the copper owing to slight roughening; and (2) the formation of caustic soda would reduce the hydrolysis of the citrate and so bring about a small increase in the citrate ion concentration.

Sodium Tartrate.—The pure recrystallized salt was used and the results are shown in fig. 1. The copper remained bright throughout the major part of the run, very slight tarnishing occurring towards the end.

Sodium Malonate.—The pure recrystallized salt was used and the results are given in fig. 2. The copper slowly became tarnished and after about 20 days had assumed a purplish tint. No separation of green compound occurred, but the purplish deposit on the copper (perhaps another type of basic salt) gradually increased in thickness until the copper was "rotted" almost completely through. The concentration of copper in solution passed through a sharp maximum. Trouble was experienced in this and other experiments through moulds growing in the solutions. To determine whether this affected the results a second series of flasks was used, greater care being taken to exclude spores. Although the growth of mould was not prevented it only occurred at a much later stage of the run. The results obtained (see fig. 2) indicated that it had little or no effect.

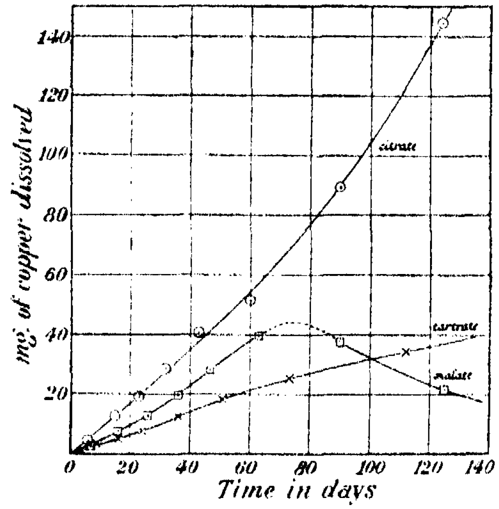

FIG. 1.

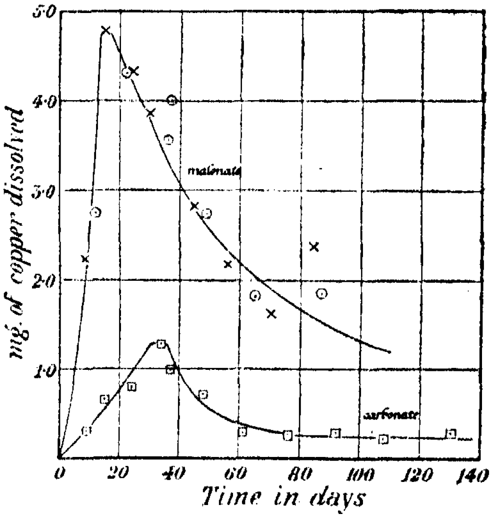

FIG. 2.

Sodium Carbonate.—The "A.R." salt was used and the results are shown in fig. 2. Dark stains developed on the copper in the course of 2 to 3 days, becoming quite black, but not completely covering the copper after 10 days. The concentration of copper in solution increased until after 30 to 40 days, a small but gradually increasing quantity of a verdigris-like precipitate was deposited on the copper and on the bottom of the flask. This precipitation was accompanied by a diminution of the concentration of dissolved copper. The formation of the black film, which was thin and firmly adherent, was probably connected with the high hydroxyl ion concentration of the carbonate solution.

Sodium Succinate.—The pure recrystallized salt was used and the results are given in fig. 3. The copper remained bright throughout, only the faintest trace of tarnishing occurring towards the end of the run. After 4 days a small quantity of a very pale blue precipitate was distinctly visible. This contained copper and was probably the sparingly soluble copper succinate, although the amount formed was insufficient to confirm this view. The concentration of copper passed through a maximum and it is possible that the subsequent fall in concentration was due to the precipitation of basic salt.

Sodium Acetate.—The "A.R." salt was used and the results are given in fig. 3. The copper remained almost untarnished for 40 to 60 days after which slight but appreciable tarnishing, accompanied by a small but definite decrease in the concentration of dissolved copper, occurred. No precipitate was formed.

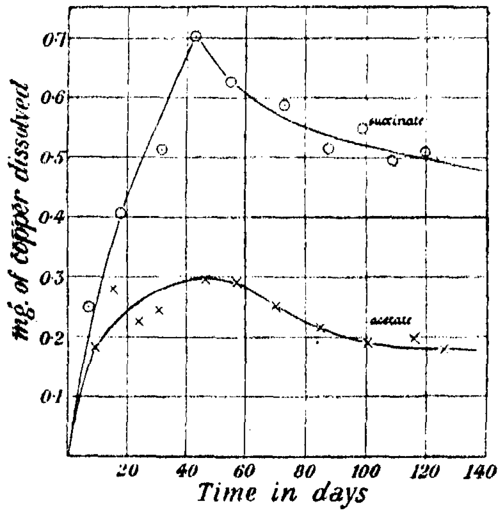

Fig. 3.

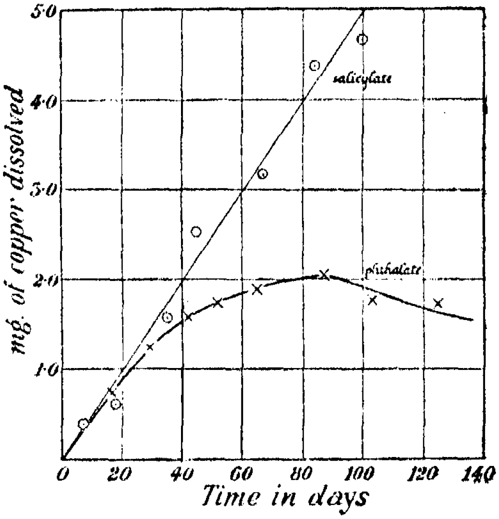

Fig. 4.

Sodium Phthalate.—The pure recrystallized salt was used and the results are given in fig. 4. They are similar to those obtained with sodium succinate, differing only in magnitude.

Sodium Salicylate.—The pure recrystallized salt was used and the results are shown in fig. 4. Only very slight tarnishing occurred towards the end of the experiment. All the above salts gave deep blue solutions, the colour varying according to the extent of the attack on the copper. With sodium salicylate, however, the solution became green. No precipitation occurred.

Sodium Benzoate.—The pure recrystallized salt was used. After 3 to 4 days, a few verdigris-like particles became visible upon the copper. These gradually grew in number until after 100 days, the metal was almost completely covered.

The copper itself remained quite bright. Analysis of the solution showed it to contain a small but reasonably constant amount of copper (about 0·1 mg.), too small to determine with a high degree of accuracy.

Summary of Results.

The rates of solution of copper in the various sodium salt solutions, determined from the initial slopes of the curves shown in figs. 1–4, are given in Table I. The third column ot the table gives the potential of the following concentration cell :—

$$\mathrm{Cu}\ \left|\ 0{\cdot}01\mathrm{M\ CuSO_4}\ \right|\ \mathrm{sat.\ KNO_3}\ \left|\ \begin{array}{c} 0{\cdot}01\mathrm{M\ CuSO_4} \\ + \\ 0{\cdot}2\mathrm{N\ NaX} \end{array}\ \right|\ \mathrm{Cu.}$$

This potential can be taken as a measure of the co-ordinating tendency of the particular anion, for it depends upon the extent of the removal of free copper ions from solution by the anion. It was not possible to carry out potential measurements with the succinate and carbonate as both these anions form very sparingly soluble copper salts. On theoretical grounds there is little doubt that the co-ordinating tendencies of these anions are less than those of the anions occurring above them in the table. Hydrolysis prevented accurate measurements being made with sodium acetate.

Table I.

Anion (0·2 N).	Rate of solution of Cu, mg./day.	P.D. of concentration cell, millivolts.
Citrate	0·82	232
Oxalate	0·45	229
Tartrate	0·34	96
Malonate	0·28	149
Salicylate	0·050	17
Phthalate	0·043	47
Succinate	0·038	—
Carbonate	0·038	—
Acetate	0·019	very small

Nickel.

The experiments employing nickel instead of copper were carried out in an exactly similar manner. No tarnishing or precipitation of basic salts occurred in any of the experiments and the extent to which the nickel dissolved was very much less than for copper. The results obtained are shown in Table II.

The phthalate, acetate, salicylate, succinate, carbonate, and benzoate solutions were examined at similar intervals. In one test, the phthalate and the acetate both showed a doubtful trace of nickel, but with all the other anions the most careful application of the dimethylglyoxime test failed to show the presence of any nickel in solution.

Table II.

	Anion (0·2 N).			
	Citrate.	Oxalate.	Tartrate.	Malonate.
mg. Ni dissolved	0·19 in 75 days	0·23 in 76 days	0·08 in 57 days	0·06 in 69 days
	0·20 in 100 days	0·34 in 101 days	0·11 in 81 days	0·04 in 94 days
	0·29 in 144 days	0·31 in 145 days	0·14 in 125 days	0·05 in 138 days

Discussion.

The above results show that both pure copper and pure nickel pass into solution when placed in aqueous solutions of certain neutral sodium salts. Copper does this to a much greater extent than nickel, although the electrolytic solution pressure of the latter is greater than that of the former. On the above theory this greater corrodibility of copper is determined by that "chemical" property of copper which governs its tendency to form sparingly dissociated complex ions. Although no quantitative data are available, it is well known that copper forms complex ions which are both more numerous and more stable than those formed by nickel.

It is significant that only those anions which bring about the relatively rapid attack of copper, viz., citrate, oxalate, tartrate, and malonate, have any appreciable attack on nickel. The order of the magnitude of the attack is not the same for both metals, but it should be remembered that with copper, film formation occurred in certain of the experiments, and this probably had a retarding effect upon the rate of attack.

For copper there is not a strict parallelism between the rate of attack and the co-ordinating tendency of the anion, as measured by the concentration cell potential. The parallelism is, however, sufficient to lend considerable support to the views here advanced. It should be remembered that film formation, particularly with the oxalate and malonate experiments, probably retards the rate of attack. It is possible also that those anions which contain hydroxyl groups, viz., citrate, tartrate, and salicylate, form a different type of complex ion from that formed by the other anions. If the rates of solution of copper brought about by those anions which are known to form the same type of complex ion, viz., oxalate, malonate, phthalate, succinate, and carbonate, are compared, it will be seen that the results are in an order which could have been predicted on theoretical grounds.

The general form of the curves in figs. 1–4 can be simply explained by the formation of insoluble basic salts as the alkalinity of the solution increases. Where the copper forms a normal salt which is sparingly soluble in excess of the sodium salt, *e.g.*, with the succinate anion, then the precipitation of the normal salt will also play a part. The citrate, tartrate, and salicylate curves do not show a maximum over the range studied. This is due to the relatively greater stability in alkaline solution of the complex ions formed, for if a weaker sodium salt solution is used or if caustic soda is added to a sodium salt solution of the same concentration, figs. 5 and 7, then sodium citrate gives a maximum in the same manner as the other salts. It is interesting to note that the citrate, tartrate, and salicylate ions all contain hydroxyl groups.

Some workers* hold that metallic corrosion in neutral solution is anodic in character and that the presence of electrolytic couples is necessary for corrosion to occur. Electrolytic couples, it is believed, are formed between the pure metal and impurities or, when the metal is pure, through "differential aeration." The results obtained prove quite conclusively that "couple action" can have little or no effect in the above type of corrosive process. Apart from the nature of the metal itself the dominant factor determining the rate of corrosion is the nature of the anion present in solution. The relatively large difference in the rates of corrosion of copper in citrate and acetate solutions cannot be satisfactorily explained by any anodic theory. Electrolytic action does undoubtedly play an important part in certain types of metallic corrosion, but the above results show that the nature of the anion present in solution may have a predominating influence. Natural waters contain anions of high co-ordinating tendency, *e.g.*, carbonate, halide, humic acid, and protein acid, which probably play an important part in corrosive processes.

The Effect of Concentration.

The rates of solution of copper in sodium citrate solutions of various concentrations were measured by a method exactly similar to the foregoing. The results are shown in figs. 5 and 6. The form of the curve, fig. 6, can be interpreted as follows. The rate of solution of the copper will be controlled by the concentration of the citrate ions and by the rate of entry of oxygen into the solution. In the more concentrated solutions, viz., 4N, 2N, 1·5N, N, and 0·75N the solute offers serious resistance to the flow of oxygen to the surface of the copper. This is retarded to such an extent in the stronger solutions that it becomes the major controlling factor. In the more dilute solutions, oxygen has freer access to the surface of the copper and the concentration of the citrate ions then exerts a major influence in determining the rate of attack. This view is supported by the form of the curves shown in fig. 5 as there is a distinct retardation in the rate of solution with the more dilute solutions. It is significant that the largest amount of copper found in the 0·001N citrate solution, viz., 1·62 mg. in 50 c.c., is almost exactly equivalent (= 0·00102 gm. equivalents per litre) to the citrate present.

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* Evans, "The Corrosion of Metals" (Arnold, 1926).

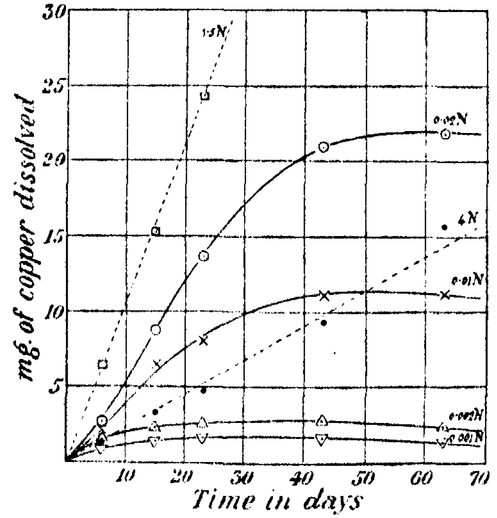

FIG. 5.

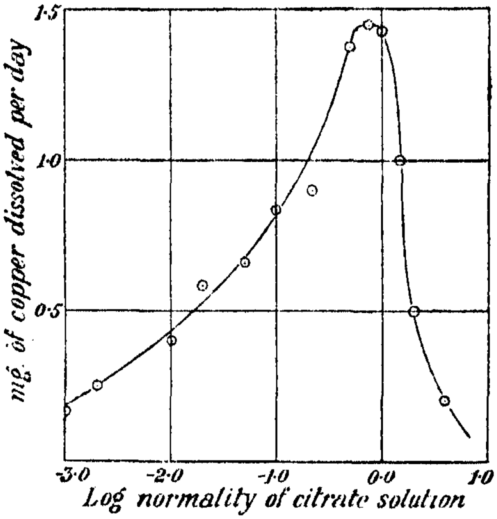

FIG. 6.

The form of the curve shown in fig. 6 is similar to that obtained by Bengough* for the rate of corrosion of steel in potassium chloride solutions of various concentration. This fact lends support to the view that the theory here advanced is of general application to corrosion phenomena.

The Effect of Acidity.

The rate of solution of copper under the standard conditions outlined above, in 0·2N citric acid, 0·2N sodium dihydrogen citrate, 0·2N sodium hydrogen citrate and in 0·2N sodium citrate + 0·2N caustic soda, has also been determined. The results are shown in fig. 7. The following points are noteworthy. The rate of corrosion in citric acid is only slightly more rapid than that in the neutral citrate solution. The neutral citrate solution dissolves the copper more rapidly than solutions of the acid salts. The rate of solution of the copper in the mixed solution of sodium citrate and caustic soda is at first almost identical with that which occurs with the citrate alone. In the alkaline solution the copper gradually became coated with a black, firmly adhering film.

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* 'J. Soc. Chem. Ind.,' vol. 52, p. 210 (1933).

The Effect of the Area of the Copper.

Experiments were also carried out with 0·2 N solutions of both sodium citrate and sodium oxalate in which pieces of copper twice, half, quarter, and one-eighth the area of the standard piece were employed. The results are shown in fig. 8. where the rate of solution of the copper has been plotted against the square root of the area of the copper. That this rate is governed, within the limits studied, by such a simple relationship, can be explained as follows. Other conditions being the same, the rate of solution of the copper must be governed by the flow of oxygen to the surface of the copper. When the area of the copper is increased, then the rate of solution cannot increase linearly, for retarding forces must come into play as an increased amount of oxygen

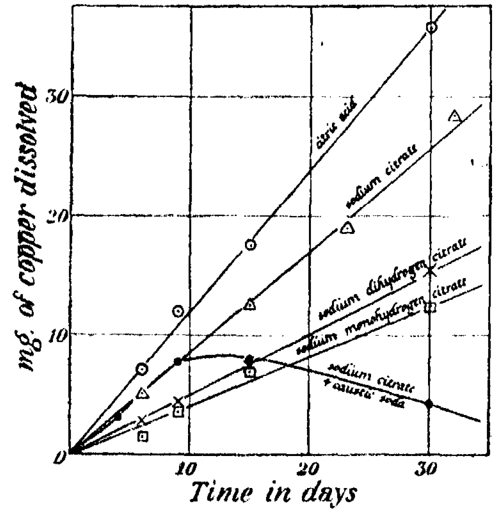

FIG. 7.

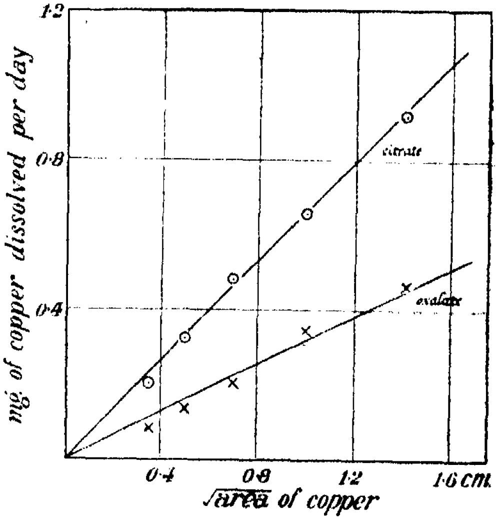

FIG. 8.

tends to pass through the same volume of solution in the same time, *i.e.*, R = K . A/R, where R = rate of solution, K = constant, and A = area of copper.

This phenomenon probably plays a part in "pitting" when the surface of a metal is imperfectly covered with a protective film, for there will be a tendency for the rate of solution per unit area to be greater, the smaller the area exposed to attack.

On the Quantum Theory of the Electromagnetic Field.

By Max Born.

(Communicated by R. H. Fowler, F.R.S.—Received August 9, 1933.)

Introduction.

Existing attempts[†] to apply the quantum theory to the electromagnetic field are open to serious objections. Above all, the time is treated differently from the space co-ordinates; the quantities defining the state (*e.g.*, field strengths) are developed in Fourier series according to their space distribution, but the Fourier coefficients are not considered as classical functions of the time but as quantum oscillators. Also the subsequent development of these principles into formulæ, in which the field quantities are operators depending on position in space, does not affect the fundamental distinction between time and space variables. This is also shown by the fact that the relativistic invariance cannot be derived simply from the symmetry of the formulæ in the four world co-ordinates, but must be artificially imposed and demonstrated by a complicated proof. Further, it is not a self-contained theory of the electromagnetic field, but a superposition of Maxwell's electromagnetic field on the material field of Schrödinger or Dirac, in which the elementary particles occur as point-charges. Thus there is no idea of the radius of the particle, and consequently no rational notion of mass, not to mention a theory of the ratio of the mass of a proton to that of an electron. In addition to these fundamental difficulties there are others, such as that of the infinitely great "Nullpunktsenergie," which is avoided by an artificial modification of the formalism.

[†] *Cf.* Rosenfeld, "La théorie quantique des champs," 'Conferences faites à l'Institut Henri Poincairé,' (1931), or Pauli, § 6, 'Handbuch d. Phys.,' 2nd ed., vol. 24.

Whether it is possible, through the generalization of the approved principles of quantum mechanics, to create a field theory agreeing with reality can first be known when this generalization has been systematically undertaken. This is attempted here. Unfortunately, the mathematical formalism is so unusual and the physical interpretation so difficult, that I have been unable to obtain results capable of test. As a preliminary the problem is to examine and distinguish between the possible methods.

I believe, however, that I have found an important result in classical electrodynamics. For the formalism shows clearly that Maxwell's equations in the original form are not compatible with the suggested quantum laws ; and they have to be replaced by another set of equations, which are a special form of Mie's general field theory. I have studied the properties of this field by classical methods, and found a number of interesting results, the chief of which is the existence of an electron with finite radius and finite energy, whose potential agrees with Coulomb's law for large distances. This electron behaves in external fields like the classical point-charge, provided that the fields are almost constant in a region large compared with the dimensions of an electron ; but it may behave quite differently for short waves. It has not yet been possible to interpret these considerations according to the quantum theory, but it seems that the new field laws may have the properties necessary to explain the inconsistencies of the older theories.

In order to bring the quantization of the field-equations (with more than one independent variable, space and time) into closer analogy with the quantization of the mechanical equations of motion (with one independent variable, time), it is necessary to reduce the process for the latter case to a form capable of generalization. The usual expositions are not entirely suitable. We begin, therefore, with a simple mechanical example, that of the motion of a particle in a plane ; and we will emphasize the properties that hold for the case of more than one independent variable.

§ 1. *Classical Mechanics of the Particle in the Plane.*

As we are concerned with a mathematical analogy, we do not retain the usual notation, but denote the time by x and the plane Cartesian co-ordinates by y and z, which are functions of x. Their differential coefficients with respect to x are denoted by y' and z'. We write the Hamiltonian Principle in complete generality as a problem in the calculus of variations,

$$\delta \int \mathrm{L}(x, y, z, y', z')\, dx = 0. \tag{1.1}$$

As yet, we do not make use of the fact that the Lagrangian is the difference of the kinetic and potential energies. The Euler-Lagrangian equations of motion are

$$\frac{d}{dx}\frac{\partial L}{\partial y'} - \frac{\partial L}{\partial y} = 0, \qquad \frac{d}{dx}\frac{\partial L}{\partial z'} - \frac{\partial L}{\partial z} = 0. \tag{1.2}$$

Now, instead of following the usual method, which is to reduce these equations to canonical form and develop the theory from the *maintenance* of this form (canonical transformation), we take another property as our starting point, namely, *Hilbert's* "*Independence Theorem.*"† We express this in the following form.

The three quantities called impulses,

$$\left.\begin{aligned} p_x &= L - y'\frac{\partial L}{\partial y'} - z'\frac{\partial L}{\partial z'}, \\ p_y &= \frac{\partial L}{\partial y'}, \\ p_z &= \frac{\partial L}{\partial z'} \end{aligned}\right\} \tag{1.3}$$

are functions of x, y, z, y', z'. Now y' and z' can always be chosen as functions of x, y, z (as spacial distribution), namely,

$$y' = \eta(x, y, z), \qquad z' = \zeta(x, y, z), \tag{1.4}$$

so that the integral

$$\begin{aligned} S &= \int (p_x dx + p_y d_y + p_z d_z) \\ &= \int \{L + p_y(y' - \eta) + p_z(z' - \zeta)\}\, dx, \end{aligned} \tag{1.5}$$

extending over a curve C in the x, y, z-space, is independent of the form of the curve and a function of the two end-points alone. This is the "action function." We have

$$\frac{\partial S}{\partial x} = p_x, \qquad \frac{\partial S}{\partial y} = p_y, \qquad \frac{\partial S}{\partial z} = p_z. \tag{1.6}$$

There are different methods for the determination of (1.4). From (1.6), we obtain

$$\frac{\partial p_z}{\partial y} - \frac{\partial p_y}{\partial z} = 0, \qquad \frac{\partial p_x}{\partial z} - \frac{\partial p_z}{\partial x} = 0, \qquad \frac{\partial p_y}{\partial x} - \frac{\partial p_x}{\partial y} = 0. \tag{1.7}$$

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† German "Unabhängigkeitssatz." I attended Hilbert's lectures on "Variationsrechnung" 30 years ago, and would not like to omit to thank my distinguished teacher for their lasting stimulation.

These are three partial differential equations for η, ζ, of which, however, essentially only two are independent, since the divergence of the left-hand sides vanishes identically. Every solution of these equations satisfies the "Independence Theorem." At the same time, the expressions (1.4) exhibit[†] intermediate integrals of the equations of motion (1.2). Conversely, a space-distribution (1.4) satisfying the "Independence Theorem" can be obtained by the elimination of the parameters from suitable families of curves with two parameters, called a "field." Finally, it is not necessary to determine the functions η, ζ, as the function S can be directly determined from a partial differential equation.

From two of the equations (1.6), namely,

$$\frac{\partial S}{\partial y} = p_y, \qquad \frac{\partial S}{\partial z} = p_z, \tag{1.8}$$

whose right-hand sides are functions of x, y, z, η, ζ, we obtain η and ζ as functions of x, y, z, $\partial S/\partial y$, $\partial S/\partial z$; and substitute these expressions for η and ζ in the first of equations (1.6). Then $p_x(x, y, z, \eta, \zeta)$ becomes a function of x, y, x, $\partial S/\partial y$, $\partial S/\partial z$, which, with its sign changed, we denote in the usual

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[†] The proof can be demonstrated by simple calculation. Using suffixes to denote differentiation, and using (1.3), the equations (1.7) can be written out in detail as follows :—

$$0 = \frac{\partial p_z}{\partial y} - \frac{\partial p_y}{\partial z} = (L_{\zeta\eta}\eta_y + L_{\zeta\zeta}\zeta_y + L_{\zeta y}) - (L_{\eta\eta}\eta_z + L_{\eta\zeta}\zeta_z + L_{\eta z}),$$

$$\begin{aligned} 0 = \frac{\partial p_x}{\partial z} - \frac{\partial p_z}{\partial x} = &(L_\eta\eta_z + L_\zeta\zeta_z + L_z) - \eta_z L_\eta - \eta(L_{\eta\eta}\eta_z + L_{\eta\zeta}\zeta_z + L_{\eta z}) \\ &- (L_{\zeta\eta}\eta_x + L_{\zeta\zeta}\zeta_x + L_{\zeta x}) - \zeta_x L_\zeta - \zeta(L_{\zeta\eta}\eta_z + L_{\zeta\zeta}\zeta_z + L_{\zeta z}), \\ 0 = \frac{\partial p_y}{\partial x} - \frac{\partial p_x}{\partial_y} = &-(L_\eta\eta_y + L_\zeta\zeta_y + L_y) + \eta_y L_\eta + \eta(L_{\eta\eta}\eta_y + L_{\eta\zeta}\zeta_y + L_{\eta y}) \\ &+ (L_{\eta\eta}\eta_x + L_{\eta\zeta}\zeta_x + L_{\eta x}) + \zeta_y L_\zeta + \zeta(L_{\zeta\eta}\eta_y + L_{\zeta\zeta}\zeta_y + L_{\zeta y}). \end{aligned}$$

Replacing the factor of η in the second equation and the factor of ζ in the first equation according to the equality exhibited in the first equation, we obtain

$$0 = L_z - \eta(L_{\zeta\eta}\eta_y + L_{\zeta\zeta}\zeta_y + L_{\zeta y}) - \zeta(L_{\zeta\eta}\eta_z + L_{\zeta\zeta}\zeta_z + L_{\zeta z}) - (L_{\zeta\eta}\eta_x + L_{\zeta\zeta}\zeta_x + L_{\zeta x}),$$
$$0 = L_y - \eta(L_{\eta\eta}\eta_y + L_{\eta\zeta}\zeta_y + L_{\eta y}) - \zeta(L_{\eta\eta}\eta_z + L_{\eta\zeta}\zeta_z + L_{\eta z}) - (L_{\eta\eta}\eta_x + L_{\eta\zeta}\zeta_x + L_{\eta x}).$$

Now, it is seen that only the four expressions

$$\eta = y', \quad \zeta = z', \quad \eta_x + \eta_y\eta + \eta_z\zeta = y'', \quad \zeta_x + \zeta_y\eta + \zeta_z\zeta = z''$$

occur. Thus

$$0 = L_z - (L_{\zeta\eta}y'' + L_{\zeta\zeta}z'' + L_{\zeta y}y' + L_{\zeta z}z' + L_{\zeta x}),$$
$$0 = L_y - (L_{\eta\eta}y'' + L_{\eta\zeta}z'' + L_{\eta y}y' + L_{\eta z}z' + L_{\eta x}),$$

which are the equations of motion (1.2) written out in detail.

manner as the Hamiltonian, $H = -p_x$. We obtain, then, the Hamilton-Jacobi differential equation,

$$\frac{\partial S}{\partial x} + H\left(x, y, z, \frac{\partial S}{\partial y}, \frac{\partial S}{\partial z}\right) = 0. \tag{1.9}$$

It is sufficient to know any general integral of the equation, *i.e.*, one which contains two constants of integration, α and β. We put

$$\frac{\partial S(x, y, z, \alpha, \beta)}{\partial \alpha} = a, \quad \frac{\partial S(x, y, z, \alpha, \beta)}{\partial \beta} = b, \tag{1.10}$$

and solve these equations for y and z. The resulting 4-parameter family of curves in the x, y, z space is identical with the totality of motions (solutions of (1.2)).† Here it has been supposed that the time x does not disappear through the differentiation in (1.10).

In the interpretation of the transformation theory, the equations (1.8) and (1.10) represent a canonical transformation with the generating function (or transformation function) S for the change from the old co-ordinates y, z and impulses p_y, p_z to the new α, β ; a, b. The function S can also be defined by the integral

$$S = \int_{x_0}^{x} L\,dx, \tag{1.11}$$

where the integration is along a path (solution of (1.2)) extending from the point $P_0(x_0, y_0, z_0)$ to the variable point $P(x, y, z)$. Then the paths starting from P_0 form a field ; and consequently the equations (1.4) hold, so that the extra terms in (1.5) disappear.‡

As an example we consider the case of no forces. Then L becomes simply the kinetic energy (the mass is taken to be unity),

$$L = \tfrac{1}{2}(y'^2 + z'^2). \tag{1A}$$

From (1.3) we obtain

$$p_x = -\tfrac{1}{2}(y'^2 + z'^2), \quad p_y = y', \quad p_z = z' ; \qquad H = \tfrac{1}{2}(p_y^2 + p_z^2), \tag{1B}$$

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† The proof of this theorem must be omitted. A good summary, and a generalization to more than one independent variable (used later), is given by Prange, "Die Hamilton-Jacobische Theorie für Doppel-Integrale," 'Göttinger Dissertation,' 1915 (W. Fr. Kaestner, Göttingen).

‡ Dirac uses the definition (1.11) of the transformation function S in an interesting paper ('Phys. Z. Sowjetunion,' vol. 3, p. 64 (1933)), in which he attempts to generalize the fundamental ideas of the transformation theory to the case of more than one independent variable. Here we take another point of view as our starting point.

and the Hamilton's equation, (1.9), becomes

$$\frac{\partial S}{\partial x} + \tfrac{1}{2}\left\{\left(\frac{\partial S}{\partial y}\right)^2 + \left(\frac{\partial S}{\partial z}\right)^2\right\} = 0. \tag{1c}$$

Every solution of this differential equation, which contains two constants, gives according to (1.10), all possible paths. We will give two solutions, and then show how and why the quantum theory favours a special form of solution.

I.—We consider first the solution

$$S = -\tfrac{1}{2}(\alpha^2 + \beta^2)\, x + \alpha y + \beta z. \tag{1E}$$

From (1.10), we have

$$\frac{\partial S}{\partial \alpha} = -\alpha x + y = a, \qquad \frac{\partial S}{\partial y} = -\beta x + z = b, \tag{1F}$$

i.e., the totality of uniform motions in straight lines

$$y = a + \alpha x, \qquad z = b + \beta x, \tag{1G}$$

as must, indeed, be the case.

II.—As our second solution, we consider

$$S = -\tfrac{1}{2}\alpha^2 x + \alpha\sqrt{(y - \beta)^2 + z^2}. \tag{1H}$$

From (1.10), we now obtain

$$\frac{\partial S}{\partial \alpha} = -\alpha x + \sqrt{(y - \beta)^2 + z^2} = a, \quad \frac{\partial S}{\partial \beta} = \alpha\frac{y - \beta}{\sqrt{(y - \beta)^2 + z^2}} = b. \tag{1K}$$

The solutions for y and z are

$$y = \frac{ab + \alpha\beta}{\alpha} + bx, \quad z = \frac{a}{\alpha}\sqrt{\alpha^2 - b^2} + \sqrt{\alpha^2 - b^2}\,.\,x, \tag{1L}$$

and again represent the totality of uniform motions in straight lines.

Apart from these two solutions, there are infinitely many other possible ways of choosing the function $S(x, y, z, \alpha, \beta)$; indeed, so many ways as there are families of surfaces with one parameter in the x, y, z-space, $f(x, y, z) = \beta$. It is only necessary to find the solutions of (1.9) which reduce to the surfaces $f(x, y, z) = \beta$ for $\alpha = 0$.

§ 2. *The Quantum Mechanics of the Particle in the Plane.*

We come now to the question of the change over to quantum mechanics. As is well known, for this there is the following formal method.

The equations (1.6) are replaced by†

$$\frac{1}{i}\frac{\partial}{\partial x} = p_x, \qquad \frac{1}{i}\frac{\partial}{\partial y} = p_y, \qquad \frac{1}{i}\frac{\partial}{\partial z} = p_z, \tag{2.1}$$

that is, the impulse components are replaced by operators, which act on functions $\psi(x, y, z)$ of space and time. Then, out of the first order differential equation (1.9) we obtain the Schrödinger differential equation,

$$\left\{\frac{1}{i}\frac{\partial}{\partial x} + \mathrm{H}\left(x, y, z, \frac{1}{i}\frac{\partial}{\partial y}, \frac{1}{i}\frac{\partial}{\partial z}\right)\right\} \psi = 0. \tag{2.2}$$

This rule has the advantage of holding for arbitrary functions L or H, but it does not display clearly the inner meaning of the process. We give, therefore, another method, which proceeds from the special case of motion under no forces. This motion is distinguished by the fact that L, and thus also H, is not an explicit function of x, y, z; according to (1A) we have

$$\mathrm{L} = \tfrac{1}{2}(y'^2 + z'^2), \qquad \mathrm{H} = \tfrac{1}{2}(p_y^2 + p_z^2). \tag{2.3}$$

Our conclusions hold also when L is an arbitrary function of y', z', *i.e.*, H is an arbitrary function of p_y and p_z.

The wave mechanics must contain the classical mechanics as a limiting case, which is obtained by introducing Planck's constant h in (2.1) and making $h \to 0$; the wave surfaces $\psi =$ constant become in this limiting case the surfaces $\mathrm{S} =$ constant, where S denotes the phase of the wave. There is thus the asymptotic connection

$$\psi \to e^{i\mathrm{S}}. \tag{2.4}$$

Here S could be any solution of equation (1C) (or, more generally, of (1.9)). Now, to change over from the limiting case to a strict wave equation, we use an entirely particular solution of (1C), namely the linear (1E),

$$\mathrm{S} = -\tfrac{1}{2}(\alpha^2 + \beta^2)\, x + \alpha y + \beta z, \tag{2.5}$$

and apply the ***principle of superposition.*** We construct the ***wave packet***

$$\psi(x, y, z) = \iint \phi(\alpha, \beta)\, e^{i[-\frac{1}{2}(\alpha^2+\beta^2)x + \alpha y + \beta z]}\, d\alpha\, d\beta, \tag{2.6}$$

having an arbitrary amplitude function $\phi(\alpha, \beta)$. The ψ satisfies identically the equation

$$\frac{1}{i}\frac{\partial\psi}{\partial x} - \tfrac{1}{2}\left(\frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = 0, \tag{2.7}$$

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† The units are chosen so that $h = 2\pi$.

i.e., the Schrödinger wave equation (2.2) with $\mathrm{H} = \frac{1}{2}(p_y^2 + p_z^2)$. Exactly the same holds for an arbitrary function $\mathrm{H}(p_y, p_z)$. The wave function

$$\psi(x, y, z) = \iint \phi(\alpha, \beta)\, e^{i[-\mathrm{H}(\alpha, \beta)x + \alpha y + \beta z]}\, d\alpha\, d\beta \tag{2.8}$$

then satisfies the equation

$$\left\{\frac{1}{i}\frac{\partial}{\partial x} + \mathrm{H}\left(\frac{1}{i}\frac{\partial}{\partial y}, \frac{1}{i}\frac{\partial}{\partial z}\right)\right\}\psi = 0. \tag{2.9}$$

Now $|\psi|^2 dy\, dz$ is the probability that the particle is in the space element $dy\, dz$ at time x.

By (2.6) the linear solutions

$$\mathrm{S} = -\mathrm{H}(\alpha, \beta)\, x + \alpha y + \beta z \tag{2.10}$$

of the Hamilton-Jacobi differential equation (1.9) are preferred to all other solutions, *e.g.*, the functions (1H) given in § 1, II. Clearly S = const., as given by (2.5), represents a plane wave, while (1B) denotes a spherical wave. Other solutions for S give waves of different forms.

Instead of taking these curved wave surfaces out of the classical mechanics and introducing them into the suitably modified equation (2.4), the wave mechanics limits itself to *plane* wave surfaces and builds up all phenomena through the superposition of elementary plane waves with variable amplitudes. This point is absolutely essential for the generalization, which we shall later attempt.

If there is a potential energy, *i.e.*, if H is a function of y and z (and possibly of the time x), as well as of p_y and p_z, then the generalization of equation (2.9) to (2.2) suggests itself; and this is justified by experience. However, for our purposes, this is not necessary.

§ 3. *The Classical Mechanics of the One-dimensional Continuum.*

We consider now a continuously extending medium, which we assume to be one-dimensional (vibrating string). There are two independent variables x, y, of which one is the time (x, say), and we look for a function $z(x, y)$. We denote differentiation again by suffixes, so that

$$z_x = \frac{\partial z}{\partial x}, \qquad z_y = \frac{\partial z}{\partial y}.$$

The Hamiltonian Principle becomes a variation problem of the form†

$$\delta \int L(x, y, z, z_x, z_y)\, dx\, dy = 0, \tag{3.1}$$

from which we obtain the equation of motion

$$\frac{\partial}{\partial x}\frac{\partial L}{\partial z_x} + \frac{\partial}{\partial y}\frac{\partial L}{\partial z_y} - \frac{\partial L}{\partial z} = 0. \tag{3.2}$$

We now formulate anew the "Independence Theorem," and define the corresponding "impulses,"

$$\left.\begin{aligned} p_x &= \frac{\partial L}{\partial z_x} \\ p_y &= \frac{\partial L}{\partial z_y} \\ p_z &= -L + z_x \frac{\partial L}{\partial z_x} + z_y \frac{\partial L}{\partial z_y} \end{aligned}\right\}, \tag{3.3}$$

which are functions of x, y, z, z_x, z_y.‡ We now consider the question whether we can attach to each point x, y, z a vector $\xi, \eta, 1$, such that these vectors are the normals to a family of surfaces with one parameter, namely,

$$z_x = \xi(x, y, z), \qquad z_y = \eta(x, y, z); \tag{3.4}$$

and further such that the integral

$$\left.\begin{aligned} S &= \iint \{p_x\, dy\, dz + p_y\, dz\, dx + p_z\, dx\, dy\} \\ &= \iint \{L + p_x(z_x - \xi) + p_y(z_y - \eta)\}\, dx\, dy \end{aligned}\right\}, \tag{3.5}$$

extending over a surface F in the x, y, z-space, should depend only on the boundary curve C of the surface, and be independent of the shape of the surface F. (The meaning of the second of equations (3.5) is immediately clear :— L, $p_x = \frac{\partial L}{\partial z_x}$, $p_y = \frac{\partial L}{\partial z_y}$ are explicit functions of $x, y, z, \xi(x, y, z), \eta(x, y, z)$, and depend on x, y, z; $z(x, y)$ is the surface F. In the first symmetrical equation (3.5) p_x, p_y, p_z are, in the same way, functions of x, y, z; further, if $d\sigma$ is the surface element of F, then

$$dy\, dz = z_x\, dx\, dy = \cos(\nu, x)\, d\sigma, \text{ etc.},$$

are the projections of $d\sigma$ on the co-ordinate planes.)

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† The formulæ in this section are numbered so that they correspond to those in §1.

‡ It should be noticed that the sign in (3.3) has been chosen opposite to that in (1.3).

As the condition of the independence of the integral S of the form of the surface F, we obtain two partial differential equations of the first order for ξ, η. The first is obtained from (3.4) by using the condition that $\frac{\partial z_x}{\partial y} = \frac{\partial z_y}{\partial x}$, so that

$$\frac{\partial \xi}{\partial y} + \eta \frac{\partial \xi}{\partial z} = \frac{\partial \eta}{\partial x} + \xi \frac{\partial \eta}{\partial z}. \tag{3.7A}$$

The second condition is obtained by equating the integral (3.5) over two different surfaces with the same boundary curve C, and enclosing a volume V. Then, using Gauss' Theorem,† the difference of the two surface integrals is equal to the volume integral of the divergence of the vector p_x, p_y, p_z over the volume V. Since the surface integrals are equal, the volume integral must vanish for any closed surface, so that its integrand

$$\frac{\partial p_x}{\partial x} + \frac{\partial p_y}{\partial y} + \frac{\partial p_z}{\partial z} = 0. \tag{3.7B}$$

If ξ, η are any solutions of equations (3.7A) and (3.7B), then the independence of the integral S of the form of the surface F is ensured. This integral has then, the form

$$S = \int (X\, dx + Y\, dy + Z\, dz), \tag{3.5A}$$

a line integral over the boundary curve C. From Stokes' Theorem we have

$$\frac{\partial Z}{\partial y} - \frac{\partial Y}{\partial z} = p_x, \quad \frac{\partial X}{\partial z} - \frac{\partial Z}{\partial x} = p_y, \quad \frac{\partial Y}{\partial x} - \frac{\partial X}{\partial y} = p_z; \tag{3.6}$$

and equation (3.7B) is identically satisfied. Three arbitrary functions X, Y, Z, which can further be subjected to the condition

$$\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} + \frac{\partial Z}{\partial z} = 0, \tag{3.7}$$

give, according to (3.6), values of p_x, p_y, p_z for which the value of S is independent of the shape of the surface F.

It can further be shown that, for each solution of the equations (3.7A) and

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† Or Green's theorem :—

$$\iiint \operatorname{div} \mathbf{A}\, dx\, dy\, dz = \iint \mathbf{A}_n\, d\sigma.$$

(3.7B), the formulæ (3.4) represent an integral of the equation of motion (3.2).[†] Conversely, a pair of functions, ξ, η, satisfying (3.7A) and (3.7B), *i.e.*, that make the integral S independent of the shape of F, can be obtained from each solution $z(x, y, a)$ of (3.2) with one parameter a. (It is only necessary to express the parameter a as a function of x, y, z, using $z = z(x, y, a)$, and then to substitute this value in $z_x = z_x(x, y, a)$ and $z_y = z_y(x, y, a)$.)

In order to make the analogy with the mechanics of a particle more apparent, we consider the function S as a special type of *functional*,[‡] namely, as a "*line-function*," and define the *derivatives of a line-function* with respect to the surface components of the boundary curve C.[§] By these latter is meant the surface areas of the projections of C on the co-ordinate planes :

$$\sigma_{yz} = \int dy\,dz, \qquad \sigma_{zx} = \int dz\,dx, \qquad \sigma_{xy} = \int dx\,dy. \tag{3.*}$$

Then, for every line integral of the form (3.5), we have clearly

$$\frac{\partial \mathrm{S}}{\partial\,(yz)} = \lim \frac{\mathrm{S}}{\sigma_{yz}} = \frac{\partial \mathrm{Z}}{\partial y} - \frac{\partial \mathrm{Y}}{\partial z}, \qquad \text{etc.,} \tag{3.**}$$

where the limit is to be taken by contracting the curve C to a point. With this symbolism we can write for (3.6)

$$\frac{\partial \mathrm{S}}{\partial\,(yz)} = p_x, \qquad \frac{\partial \mathrm{S}}{\partial\,(zx)} = p_y, \qquad \frac{\partial \mathrm{S}}{\partial\,(xy)} = p_x, \tag{3.6A}$$

in complete analogy with (1.6).

[†] The proof is simply a matter of calculation. Denoting differentiation by suffixes, equation (3.7B) can be written in detail as follows :—

$$\begin{aligned} 0 &= \frac{\partial}{\partial x}\mathrm{L}_\xi + \frac{\partial}{\partial y}\mathrm{L}_\eta + \frac{\partial}{\partial z}(-\mathrm{L} + \xi\mathrm{L}_\xi + \eta\mathrm{L}_\eta) \\ &= \mathrm{L}_{\xi x} + \mathrm{L}_{\xi\xi}\xi_x + \mathrm{L}_{\xi\eta}\eta_x + \mathrm{L}_{\eta y} + \mathrm{L}_{\eta\xi}\xi_y + \mathrm{L}_{\eta\eta}\eta_y \\ &\qquad - \mathrm{L}_z + \xi\,(\mathrm{L}_{\xi z} + \mathrm{L}_{\xi\xi}\xi_z + \mathrm{L}_{\xi\eta}\eta_z) + \eta\,(\mathrm{L}_{\eta z} + \mathrm{L}_{\eta\xi}\xi_z + \mathrm{L}_{\eta\eta}\eta_z). \end{aligned}$$

Now it is seen that only the five expressions

$$\begin{aligned} &\xi = z_x, && \eta = z_y, \\ &\xi_x + \xi_z\xi = z_{xx}, && \eta_y + \eta_z\eta = z_{yy}, \\ &\xi_y + \zeta_z\eta = \eta_x + \eta_z\xi = z_{xy} \end{aligned}$$

occur. Thus

$$\begin{aligned} 0 = (&\mathrm{L}_{\xi\xi}z_{xx} + \mathrm{L}_{\xi\eta}z_{xy} + \mathrm{L}_{\xi z}z_x + \mathrm{L}_{\xi x}) \\ &+ (\mathrm{L}_{\eta\eta}z_{yy} + \mathrm{L}_{\eta\xi}z_{xy} + \mathrm{L}_{\eta z}z_y + \mathrm{L}_{\xi y}) - \mathrm{L}_z, \end{aligned}$$

which is the equation of motion (3.2) written out in detail.

[‡] "Functional" means function of a function.

[§] *Cf.* Prange (*loc. cit.*), where reference is made to further literature on the subject.

Let us suppose again that ξ and η are determined as functions of x, y, z, p_x, p_y from the first two equations (3.3), and then substituted in the right-hand side of the third equation. This will give a function $-\mathrm{H}(x, y, z, p_x, p_y)$ for p_z. By introducing the expressions (3.6A) into $p_z = -\mathrm{H}(x, y, z, p_x, p_y)$, we obtain the analogy to the Hamilton-Jacobi differential equation

$$\frac{\partial \mathrm{S}}{\partial (xy)} + \mathrm{H}\left(x, y, z, \frac{\partial \mathrm{S}}{\partial (yz)}, \frac{\partial \mathrm{S}}{\partial (zx)}\right) = 0\,; \tag{3.9}$$

though this is not a partial differential equation in the ordinary sense, but a functional differential equation.†

It can be shown (Prange, *loc. cit.*) that the analogy is capable of further development, for the totality of motions (solutions of (3.2)) can be obtained through functional differentiation, analogous to (1.10), from special solutions of (3.9) with arbitrary functions. This theory is most complicated, and does not appear to have facilitated the practical integration, as was the case in the mechanics of a particle. However, the possibility of developing a comparatively simple method for the quantization depends on the same ideas as were used in § 2 ; namely, that for " force-free " systems only entirely special solutions (linear solutions) of (3.9) are necessary, and that all others can be constructed by the help of the principle of superposition.

§ 4. *A Suggested Quantum Mechanics of the One-dimensional Continuum.*

A pure field theory corresponds to a force-free continuum in the mechanical sense. If there is only action through a medium, H can depend only on the

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† In addition to satisfying this principal equation (3.9), the line-function S must satisfy two more conditions, which are obtained from (3.7A) and (3.7B). These are

$$\begin{aligned}
&\frac{\partial^2 \mathrm{H}}{\partial p_x\, \partial y} + \frac{\partial^2 \mathrm{H}}{\partial p_x^{\,2}} \frac{\partial^2 \mathrm{S}}{\partial y\, \partial (yz)} + \frac{\partial^2 \mathrm{H}}{\partial p_x\, \partial p_y} \frac{\partial^2 \mathrm{S}}{\partial y\, \partial (zx)} \\
&\qquad - \frac{\partial \mathrm{H}}{\partial p_y}\left(\frac{\partial^2 \mathrm{H}}{\partial p_x\, \partial z} + \frac{\partial^2 \mathrm{H}}{\partial p_x^{\,2}} \frac{\partial^2 \mathrm{S}}{\partial z\, \partial (yz)} + \frac{\partial^2 \mathrm{H}}{\partial p_x\, \partial p_y} \frac{\partial^2 \mathrm{S}}{\partial z\, \partial (zx)}\right) \\
&= \frac{\partial^2 \mathrm{H}}{\partial p_y\, \partial x} + \frac{\partial^2 \mathrm{H}}{\partial p_y\, \partial p_x} \frac{\partial^2 \mathrm{S}}{\partial x\, \partial (yz)} + \frac{\partial^2 \mathrm{H}}{\partial p_y^{\,2}} \frac{\partial^2 \mathrm{S}}{\partial x\, \partial (zx)} \\
&\qquad - \frac{\partial \mathrm{H}}{\partial p_x}\left(\frac{\partial^2 \mathrm{H}}{\partial p_y\, \partial z} + \frac{\partial^2 \mathrm{H}}{\partial p_y\, \partial p_z} \frac{\partial \mathrm{S}}{\partial z\, \partial (yz)} + \frac{\partial^2 \mathrm{H}}{\partial p_{yz}} \frac{\partial^2 \mathrm{S}}{\partial z\, \partial (zx)}\right)
\end{aligned} \tag{3.9A}$$

and

$$\frac{\partial^2 \mathrm{S}}{\partial x\, \partial (yz)} + \frac{\partial^2 \mathrm{S}}{\partial y\, \partial (zx)} + \frac{\partial^2 \mathrm{S}}{\partial z\, \partial (xy)} = 0, \tag{3.9B}$$

where the meaning of the second derivatives are apparent from the definition (3.**).

In what follows these conditions play no part, as they are identically fulfilled for linear line-functions.

field quantities p_x, p_y, and not explicitly on the time x and the co-ordinates y, z. Then equation (3.9) becomes

$$\frac{\partial S}{\partial (xy)} + H\left(\frac{\partial S}{\partial (yz)}, \frac{\partial S}{\partial (zx)}\right) = 0\,; \tag{4.1}$$

and a solution is immediately obtainable, namely,

$$S = \alpha\sigma_{yz} + \beta\sigma_{zx} - H(\alpha, \beta)\sigma_{xy}, \tag{4.2}$$

where α, β are arbitrary constants, and σ_{xy}, etc., are the surface components defined by (3.*). Here the functional derivatives are clearly the usual derivatives:

$$\frac{\partial S}{\partial (yz)} = \frac{\partial S}{\partial \sigma_{yz}} = \alpha, \text{ etc.} \tag{4.3}$$

This is shown by writing S explicitly as a line-integral. We use the formulæ

$$\sigma_{yz} = \int dy\, dz = \tfrac{1}{2}\int (y dz - z dy), \text{ etc.,}$$

for the surface components; and, writing $\gamma = -H(\alpha, \beta)$, we have

$$S = \tfrac{1}{2}\int \{\alpha\,(y\,dz - z\,dy) + \beta\,(z\,dx - x\,dz) + \gamma\,(x\,dy - y\,dx)\}$$

$$= \int (X\,dx + Y\,dy + Z\,dz),$$

where

$$X = \tfrac{1}{2}(\beta z - \gamma y), \qquad Y = \tfrac{1}{2}(\gamma x - \alpha z), \qquad Z = \tfrac{1}{2}(\alpha y - \beta x).$$

Thus, using (3.**), we obtain

$$\frac{\partial S}{\partial (yz)} = \frac{\partial Z}{\partial y} - \frac{\partial Y}{\partial z} = \alpha, \text{ etc.,}$$

in accordance with (4.3).

We now apply the ideas, already developed in § 2 for the mechanics of a particle, to field theory. All possible quantum states of the field are obtained by the superposition of states of the form

$$e^{i(\alpha\sigma_{yz} + \beta\sigma_{zx} - H(\alpha,\beta)\sigma_{xy})}\,;$$

that is, they are represented by integrals

$$\psi(\sigma_{yz}, \sigma_{zx}, \sigma_{xy}) = \iint \phi(\alpha, \beta)\, e^{i(\alpha\sigma_{yz} + \beta\sigma_{zx} - H(\alpha,\beta)\sigma_{xy})}\, d\alpha\, d\beta. \tag{4.4}$$

The question now is whether this hypothetical statement is capable of a physical interpretation. ψ is a line-function, because σ_{yz}, etc., are line-functions. $|\psi|^2 \, d\sigma_{yz} \, d\sigma_{zx}$ is the probability that, for given σ_{xy}, the surface components σ_{yz}, σ_{zx} lie in a definite interval $d\sigma_{yz}$, $d\sigma_{zx}$. Here σ_{xy} is the size of the space-time region;

$$\sigma_{yz} = \int dy\, dz = \int \frac{\partial z}{\partial x}\, dx\, dy = \int \{z(x_1, y) - z(x_2, y)\}\, dy$$

can be interpreted as the integral of the field-quantity $\partial z/\partial x$ over σ_{xy}, or as the space integral of the increase of z on parallels to the time-axis (x-axis); and there is a similar interpretation for σ_{zx}.

If the theory proposed here is correct, it must be pointless to fix the probability of a field state more exactly than by these data†. But that is in no way evident, and will require serious investigation. Here only the formal side of the problem will be developed.

ψ satisfies the differential equation

$$\left\{\frac{1}{i}\frac{\partial}{\partial (xy)} + \mathrm{H}\left(\frac{1}{i}\frac{\partial}{\partial (yz)}, \frac{1}{i}\frac{\partial}{\partial (zx)}\right)\right\} \psi = 0, \tag{4.5}$$

which, according to (4.3), is not a functional equation, but a partial differential equation of the usual type. We remark that the extension to "non-force-free" problems, where H contains also x, y, z, appears to be exceedingly difficult; for the meaning of "second functional derivatives," *e.g.*, $\partial^2/\partial(yz)^2$ which then occur, is not immediately clear.

Special difficulties characterize the calculation of definite mean values, which are given in the mechanics of a particle by matrix elements; for, in the space of the line-functions, the notion of an integral is not defined. We do not go further into this point here.

In comparison with this, the question of the invariance of the relativistic transformations is trivial, on account of the symmetry in x and y. For, if H is invariant for linear substitutions which change $x^2 - y^2$ into itself, so also is the equation (4.5).

§ 5. *Generalization to the Electromagnetic Field.*

We indicate, now, how the proposed formalism can be generalized to the electromagnetic field. There are four independent variables,

$$x_0 = it, \quad x_1 = x, \quad x_2 = y, \quad x_3 = z, \qquad (x_4 = ix_0 = ict), \tag{5.1}$$

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† The theory of Heisenberg and Pauli can be considered as the special case, where σ_{xy} is a rectangle with an infinitely small base dy (space) and a finite height x (time).

and four dependent variables, the potentials

$$\phi_0, \quad \phi_1, \quad \phi_2, \quad \phi_3, \qquad (\phi_4 = i\phi_0). \tag{5.2}$$

We write

$$\phi_{kl} = \partial\phi_k/\partial x_l \qquad (k, l = 1, 2, 3, 4). \tag{5.3}$$

Now the Lagrangian depends only on the antisymmetrical combinations of the ϕ_{kl}, namely, on the field-strengths

$$f_{kl} = \phi_{lk} - \phi_{kl} = -f_{lk}; \tag{5.4}$$

so that

$$\mathrm{L} = \tfrac{1}{2} \sum_{k>l} f_{kl}^2 = \tfrac{1}{4} \sum_{k,l} f_{kl}^2. \tag{5.5}$$

The "six-vector" (anti-symmetrical tensor), f_{kl}, can be split up into magnetic and electric field-strengths,

$$\mathbf{H} = (f_{23}, f_{31}, f_{12}), \qquad \mathbf{E} = i(f_{14}, f_{24}, f_{34}), \tag{5.6}$$

so that we can also write

$$\mathrm{L} = \tfrac{1}{2}(\mathbf{H}^2 - \mathbf{E}^2). \tag{5.5A}$$

Constructing the impulses in analogy to (3.3), we have

$$p_{kl} = \partial\mathrm{L}/\partial\phi_{kl} = \partial\mathrm{L}/\partial f_{kl} = f_{kl}. \tag{5.7A}$$

The impulse corresponding to the independent variables is denoted as a function of the ϕ_{kl} by p_0, or as a function of the p_{kl} by $-$ H. It is easily seen that

$$p_0 = \tfrac{1}{2} \sum_{k>l} f_{kl}^2 = \mathrm{L}, \tag{5.7B}$$

i.e.,

$$p_0 = -\mathrm{H} = \tfrac{1}{2} \sum_{k>l} p_{kl}^2 = \tfrac{1}{2}(\mathbf{H}^2 - \mathbf{E}^2). \tag{5.7C}$$

The Hamilton-Jacobi theory refers here to an 8-dimensional x_1, x_2, x_3, x_4, ϕ_1, ϕ_2, ϕ_3, ϕ_4-space. The "independent integral" is over a four dimensional manifold R_4 and is

$$\mathrm{S} = \int \left\{ p_0\, dx + \sum_{k>l} p_{kl} \left(d\phi_k\, dx^{(l)} - d\phi_l\, dx^{(k)}\right) \right\} \quad (k, l = 1, 2, 3, 4), \tag{5.8}$$

where[†]

$$dx = (1/i)\, dx_1\, dx_2\, dx_3\, dx_4 = dx_0\, dx_1\, dx_2\, dx_3,$$

[†] The factor $1/i$ is added to make S real.

and $dx^{(l)}$ is obtained from this by omitting the factor dx_l. The region of integration is thus determined by the seven components

$$\sigma_0 = 1/i \int dx = \int dx_0\, dx_1\, dx_2\, dx_3,$$

$$\sigma_{kl} = 1/i \int (d\phi_k\, dx^{(l)} - d\phi_l\, dx^{(k)}) = 1/i \int \left(\frac{\partial \phi_k}{\partial x_l} - \frac{\partial \phi_l}{\partial x_k}\right) dx = i \int f_{kl}\, dx, \tag{5.9}$$

the σ_{kl} being the integrals of the field-strengths over the space-time region σ_0.

The quantity S satisfies the Hamilton-Jacobi differential equation

$$\frac{\partial S}{\partial \sigma_0} - \tfrac{1}{2} \sum_{k>l} \left(\frac{\partial S}{\partial \sigma_{kl}}\right)^2 = 0. \tag{5.10}$$

The change over to the quantum theory is obtained as before, namely, by constructing the linear solutions of (5.10) and using them as phases of elementary waves, from which wave packets ψ are built up. These satisfy the functional differential equation of the second order, which is obtained from (5.7C) by interpreting p_0 and p_{kl} (the components of **H** and **E**) as functional differential operators:

$$p_0 = \frac{1}{i} \frac{\partial}{\partial \sigma_0}, \qquad p_{kl} = \frac{1}{i} \frac{\partial}{\partial \sigma_{kl}}, \tag{5.11}$$

or

$$\mathbf{H} = \frac{1}{i}\left(\frac{\partial}{\partial \sigma_{23}}, \frac{\partial}{\partial \sigma_{31}}, \frac{\partial}{\partial \sigma_{12}}\right), \qquad \mathbf{E} = \frac{1}{i}\left(\frac{\partial}{\partial \sigma_{14}}, \frac{\partial}{\partial \sigma_{24}}, \frac{\partial}{\partial \sigma_{34}}\right). \tag{5.11A}$$

We have then

$$(p_0 - \tfrac{1}{2} \sum_{k>l} p_{kl}^2)\, \psi = \{p_0 - \tfrac{1}{2}(\mathrm{H}^2 - \mathrm{E}^2)\}\, \psi = 0. \tag{5.12}$$

I am convinced, however, that in this form the theory is false, and indeed for a variety of reasons. Firstly there is a mathematical reason. In (5.12) occur second order functional derivatives $\partial^2/\partial\sigma_{kl}\partial\sigma_{mn}$, whose meaning is obscure. Secondly there are physical reasons. The existence of the electron (and proton) radius must be contained in the theory; here that is not so. The reason for this cannot lie in the quantization, which is only an undulatory modification of the classical formulæ for the "independent integral," but must lie in Maxwell's equations themselves. Indeed, these already fail in the classical treatment, in so far as naturally (without additional hypotheses) they only permit *point* elementary charges with infinite energy. It thus seems necessary to replace Maxwell's equations by some others. These will be constructed in the following § 6, and first treated according to classical methods.

§ 6. *Construction of New Field-equations, and their Classical Treatment.*

I suggest that, instead of the Lagrangian (5.5), the following function should be taken† :

$$\mathrm{L} = \frac{1}{a^2}\sqrt{1 + a^2\mathrm{F}}, \tag{6.1}$$

where

$$\mathrm{F} = \sum_{k > l} f_{kl}{}^2. \tag{6.2}$$

Here a is a constant of the dimensions of a reciprocal field-strength, and its size depends on the accidental choice of units for potential or field-strength.

Developing L in powers of a,

$$\mathrm{L} = \frac{1}{a^2} + \tfrac{1}{2}\mathrm{F} + \dots,$$

we see that, as a first approximation, the new L differs from the old (5.5) only by a constant term.‡

We construct the impulses

$$p_{kl} = \frac{\partial \mathrm{L}}{\partial f_{kl}} = \frac{f_{kl}}{\sqrt{1 + a^2\mathrm{F}}}; \tag{6.3}$$

these, just as the f_{kl}, are antisymmetric. They can be regarded as the " excitation " of the field f_{kl}. In order to bring the notation into accordance with the notation in Maxwell's theory of material bodies, we must write

$$\left.\begin{aligned} \mathbf{B} &= (f_{23}, f_{31}, f_{12}) & \mathbf{E} &= i\,(f_{14}, f_{24}, f_{34}) \\ \mathbf{H} &= (p_{23}, p_{31}, p_{12}) & \mathbf{D} &= -\,i\,(p_{14}, p_{24}, p_{34}) \end{aligned}\right\} \tag{6.3A}$$

The field-equations, which are derived from $\delta \int \mathrm{L}\,dx = 0$, are

$$\sum_l \frac{\partial f_{kl}}{\partial x_l} = 0. \tag{6.4A}$$

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† Mie (' Ann. Physik,' vol. 37, p. 511, vol. 39, p. 1, vol. 40, p. 1) first showed the possibility of the generalization of Maxwell's theory through the choice of L as an arbitrary function of the f_{kl} ; the difference between his theory and that suggested here is that Mie assumed L was also a function of the ϕ_k. Then he defined the densities of charge and current as the derivatives of L with respect to the ϕ_k. But this assumption leads to serious difficulties, because it is physically impossible that the laws of the field should depend on the absolute value of the potentials (see the critical remarks on Mie's theory by Pauli, " Relativitätstheorie " ; ' Encycl. Math. Wiss.,' vol. 19, p. 758). In our theory this difficulty is avoided.

‡ This is not quite immaterial ; indeed, it causes the space integral of L to be infinite in the statical case. In the treatment of the stationary electron (§ 7), it must therefore be subtracted from L.

In addition, from (5.4), we have the identities

$$\sum_{l} \frac{\partial f^*_{kl}}{\partial x_l} = 0, \tag{6.4B}$$

where f^* is the *dual* tensor of f, obtained by changing the suffixes 23, 31, 12 with 14, 24, 34 respectively.

The tensors (six-vectors) f and p can now be treated completely symmetrically. For this purpose, we use Legendre's transformation

$$p_{kl} = \frac{\partial \mathrm{L}}{\partial f_{kl}}, \qquad \mathrm{H} = -\mathrm{L} + \sum_{k>l} p_{kl} f_{kl}, \tag{6.5}$$

in which L is regarded as a function of the six independent variables f_{kl}. Thus the p_{kl} are functions of the f_{kl}, and L is so chosen that conversely the f_{kl} are functions of the p_{kl}. Then H can be regarded as a function of the p_{kl}, and we have

$$d\mathrm{H} = \sum_{k>l} f_{kl}\, dp_{kl},$$

or

$$f_{kl} = \frac{\partial \mathrm{H}}{\partial p_{kl}}. \tag{6.6}$$

We can write (6.5) as

$$\mathrm{H} + \mathrm{L} = -\sum_{k>l} f_{kl} p_{lk} = -\sum_{k>l} f^*_{kl} p^*_{lk} = \mathrm{BH} + \mathrm{ED}. \tag{6.7}$$

This holds for any function L. Taking the special form (6.1) of L, it follows from (6.3) that

$$\mathrm{P} = \sum_{k>l} p_{kl}^2 = \frac{\mathrm{F}}{1 + a^2\mathrm{F}}, \tag{6.8}$$

or

$$(1 - a^2\mathrm{P})(1 + a^2\mathrm{F}) = 1. \tag{6.9}$$

Further, from (6.7),

$$\mathrm{H} = -\frac{1}{a^2}\sqrt{1 - a^2\mathrm{P}}. \tag{6.10}$$

According to (6.8) it is clear that P is invariant for the interchange of the tensor p with its dual tensor, so that

$$\mathrm{P} = \sum_{k>l} p^{*2}_{kl}. \tag{6.8A}$$

We can thus write the equations (6.4B) and (6.4A) as

$$\sum_{l} \frac{\partial f^*_{kl}}{\partial x_l} = 0, \tag{6.4C}$$

and

$$\sum_{l} \frac{\partial (p^{*}{}_{kl})^{*}}{\partial x_l} = 0. \tag{6.4D}$$

The equations (6.4D) show that there are four "anti-potentials," Φ_1, Φ_2, Φ_3, Φ_4, such that

$$p^{*}{}_{kl} = \frac{\partial \Phi_l}{\partial x_k} - \frac{\partial \Phi_k}{\partial x_l}; \tag{6.11}$$

and then (6.4C) are the field equations for the variational equation

$$\delta \int \mathrm{H}\, dx = 0,$$

where the Φ_k are the unknown functions, and the f_{kl} are defined by (6.6), or

$$f^{*}{}_{kl} = \frac{\partial \mathrm{H}}{\partial p^{*}{}_{kl}}. \tag{6.6A}$$

We derive now the laws corresponding to the Laws of Conservation of Energy and Impulse in Maxwell's theory. They are a consequence of the fact that L does not depend on the independent variables x_1, x_2, x_3, x_4.† Thus we have

$$\frac{\partial \mathrm{L}}{\partial x_j} = \sum_{k>l} p_{kl} \frac{\partial f_{kl}}{\partial x_j} = \tfrac{1}{2} \sum_{k,l} p_{kl} \left(\frac{\partial^2 \phi_l}{\partial x_j\, \partial x_k} - \frac{\partial^2 \phi_k}{\partial x_j\, \partial x_l} \right)$$
$$= - \sum_{k,l} p_{kl} \frac{\partial^2 \phi_k}{\partial x_j\, \partial x_l}.$$

On the other hand, it follows from (6.4A) by multiplication with $\partial \phi_k / \partial x_j$ and summation over k that

$$\sum_{k,l} \frac{\partial \phi_k}{\partial x_j} \frac{\partial p_{kl}}{\partial x_l} = 0.$$

The last two equations give

$$\frac{\partial \mathrm{L}}{\partial x_j} = - \sum_{k,l} \frac{\partial}{\partial x_l} \left(p_{kl} \frac{\partial \phi_k}{\partial x_j} \right). \tag{6.12}$$

Since p_{kl} is anti-symmetric, we have the trivial identity

$$\sum_{k,l} p_{kl} \frac{\partial^2 \phi_j}{\partial x_k\, \partial x_l} = 0.$$

From (6.4A) it follows from multiplication with $\partial \phi_j / \partial x_k$ and summation over k that

$$\sum_{k,l} \frac{\partial p_{kl}}{\partial x_l} \frac{\partial \phi_j}{\partial x_k} = 0.$$

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† Born, 'Gött. Nachr.,' p. 1 (1914).

Adding this to the last equation, we obtain

$$\sum_{k,l} \frac{\partial}{\partial x_l}\left(p_{kl}\frac{\partial \phi_j}{\partial x_k}\right) = 0.$$

This combined with (6.12) gives

$$\sum_l \frac{\partial}{\partial x_l}\left(\mathrm{L}\delta_{lj} - \sum_k p_{lk} f_{kj}\right) = 0. \tag{6.13A}$$

These equations are given by Mie. He interpreted the quantities in brackets as components of the energy-tension tensor. This is, however, somewhat arbitrary.

Starting from the fact that H(p) does not depend explicitly on the x_l, it can be shown in exactly the same way that

$$\sum_l \frac{\partial}{\partial x_l}\left(\mathrm{H}\delta_{lj} - \sum_k f^*_{lk} p^*_{kj}\right) = 0. \tag{6.13B}$$

The quantities in the brackets are, however, different from those occurring in (6.13A). *Any* linear combination could be interpreted as a component of the energy-tension tensor. The most reasonable seems to me to be to take the half-differences

$$\mathrm{T}_{lj} = \tfrac{1}{2}(\mathrm{L} - \mathrm{H})_{lj} - \tfrac{1}{2}\sum_{k>l}\left(p_{lk} f_{kj} - f^*_{lk}\, p^*_{kj}\right). \tag{6.14}$$

For, in the limit $a \to 0$, L − H $\to 0$, and the sum is identical with the Maxwell-Pointing components. For example, the energy density of the field is

$$\mathrm{T}_{44} = \tfrac{1}{2}(\mathrm{L} - \mathrm{H}) + \tfrac{1}{2}(\mathbf{HB} + \mathbf{ED}) \to \tfrac{1}{2}(\mathbf{H}^2 + \mathbf{E}^2). \tag{6.14A}$$

But the space integral of this is *not* connected with the mass according to Einstein's relation $\mathrm{E} = mc^2$, as we shall show in the next section. Einstein's formula depends essentially on the supposition of *linear* field-equations, and must be replaced in our theory by some other, which is only different in the matter of numerical factors. However, it always holds in its original form when it is a question of the interaction of particles (of mass m) with weak fields (of energy E).

§ 7. *Classical Treatment of the Stationary Electron.*

We show that the field equations (6.4A) and (6.4B) have electrostatic solutions, *i.e.*, solutions for which

$$\phi_1 = \phi_2 = \phi_3 = 0. \tag{7.1}$$

Putting $\phi_4 = i\phi$, we have

$$\mathbf{B} = 0, \qquad \mathbf{E} = -\left(\frac{\partial\phi}{\partial x}, \frac{\partial\phi}{\partial y}, \frac{\partial\phi}{\partial z}\right) = -\operatorname{grad}\phi. \tag{7.1A}$$

Thus

$$\mathrm{L} = \frac{1}{a^2}\sqrt{1 - a^2\mathbf{E}^2} = \frac{1}{a^2}\sqrt{1 - a^2(\operatorname{grad}\phi)^2}. \tag{7.2}$$

The equation of motion is

$$\operatorname{div}\mathbf{D} = 0, \quad \mathrm{D}_x = \frac{\partial\mathrm{L}}{\partial\mathrm{E}_x} = \frac{\mathrm{E}_x}{\sqrt{1 - a^2\mathbf{E}^2}} = \frac{-\partial\phi/\partial x}{\sqrt{1 - a^2(\operatorname{grad}\phi)^2}}. \tag{7.3}$$

From this it follows that the surface integral for the charge,

$$4\pi e = \int \mathrm{D}_r\, d\sigma, \tag{7.4}$$

vanishes, only when D is everywhere continuous.

We show, now, that there are solutions with singularities for which D is discontinuous but not infinite. For this purpose we consider the case of spherical symmetry, *i.e.*, ϕ is a function of $r = \sqrt{x^2 + y^2 + z^2}$. Then (7.2) and (7.3) reduce to

$$\mathrm{L} = \frac{1}{a^2}\sqrt{1 - a^2\mathrm{E}_r^2} = \frac{1}{a^2}\sqrt{1 - a^2\phi'^2}, \tag{7.2A}$$

$$\frac{d}{dr}(r^2\mathrm{D}_r) = 0, \qquad \mathrm{D}_r = \frac{\mathrm{E}_r}{\sqrt{1 - a^2\mathrm{E}_r^2}} = \frac{-\phi'}{\sqrt{1 - a^2\phi'^2}}. \tag{7.3A}$$

It follows that

$$r^2\mathrm{D}_r = e, \tag{7.4A}$$

where e is a constant of integration, which according to (7.4) must be interpreted as a charge.

Further integration of (7.3A) with (7.4A) gives

$$\phi = \frac{e}{r_0}\int_{r/r_0}^{\infty}\frac{dx}{\sqrt{1 + x^4}}, \tag{7.5}$$

where r_0 is defined by

$$r_0 = \sqrt{ae},$$

i.e.,

$$a = r_0^2/e, \tag{7.6}$$

and the limits of integration have been chosen so that ϕ vanishes as $r \to \infty$. For large r Coulomb's law holds asymptotically,

$$\phi \to e/r \quad \text{as} \quad r \to \infty. \tag{7.5A}$$

The function ϕ is everywhere finite, continuous, and differentiable, with the exception of the origin. There ϕ itself is still finite and has the value

$$\phi(0) = b\,e/r_0, \tag{7.7}$$

where[†]

$$b = \int_0^\infty \frac{dx}{\sqrt{1+x^4}} = 2\int_0^1 \frac{dx}{\sqrt{1+x^4}} = 2\int_1^\infty \frac{dx}{\sqrt{1+x^4}} = 1.85407;$$

but the components of **E** and **D** are discontinuous for $r = 0$. For $D_r = e/r^2$ becomes infinite, and in

$$E_r = -\phi' = \frac{e}{r_0}\frac{1}{\sqrt{1+(r/r_0)^4}}, \tag{7.8}$$

the positive value of the square root must be taken, so that the components E_x, E_y, E_z have a discontinuity of $2\,e/r_0$ on passage through the origin.

We can write ϕ as

$$\phi(r) = \frac{e}{r_0}\left(\int_{r/r_0}^1 \frac{dx}{\sqrt{1+x^4}} + \frac{b}{2}\right) = \frac{e}{r_0}\left(\int_1^{r/r_0} \frac{dx}{\sqrt{1+x^4}} + \frac{b}{2}\right),$$

so that

$$\phi\left(\frac{r_0^2}{r}\right) = \frac{e}{r_0}\left(\int_1^{r/r_0} \frac{dx}{\sqrt{1+x^4}} + \frac{b}{2}\right).$$

It follows from addition that

$$\phi(r_1) + \phi(r_2) = \phi(0) = b\,e/r_0 \quad \text{for} \quad r_1 r_2 = r_0^2. \tag{7.9}$$

The behaviour of the function $\phi(r)$ in the "interior" of the electron[‡] of radius r_0 can be obtained from its "external" behaviour with the help of the above transformation.

All formulæ are relativistically invariant. Thus the field of the uniformly moving electron can be immediately written down. For uniform motions in external fields, naturally we can only set up approximate laws. We will work out the first approximation for a spacially constant (or almost constant) field.

The existence of an external field $f_{kl}^{(e)}$ with the potentials $\phi_k^{(e)}$ means, in our theory, that a solution must be looked for such that $f_{kl} \to f_{kl}^{(e)}$ asymptotically

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[†] The integral can be expressed in terms of the ordinary elliptic integrals, *e.g.*, by the period $\omega(g_2, g_3)$ of the Weierstrassian $\wp$-function $b = \omega(-4, 0)$; also with the help of the Jacobian elliptic integrals:

$$b = F(\sin \pi/4) = \int_0^{\pi/2} \frac{d\phi}{\sqrt{1 - \sin^2 \pi/4 \,.\, \sin^2\phi}}.$$

[‡] With regard to the charge density ($4\pi\rho = \operatorname{div} \mathbf{D}$) the electron is a point; the finite radius is a property of the potential.

Table I.†—The function $\phi(x) = \int_x^\infty dy/\sqrt{1+y^4}$.

x.	$\phi(x)$.	x.	$\phi(x)$.
0	1·854	∞	0
0·1	1·754	10·00	0·100
0·2	1·654	5·00	0·200
0·3	1·554	3·33	0·300
0·4	1·455	2·50	0·399
0·5	1·357	2·00	0·497
0·6	1·262	1·67	0·592
0·7	1·169	1·43	0·685
0·8	1·082	1·25	0·772
0·9	1·000	1·11	0·854
1·0	0·927	1·00	0·927

for large distances. It follows that we must determine $\phi'_k = \phi_k - \phi_k^{(e)}$ so that $f'_{kl} = \phi'_{lk} - \phi'_{kl} \rightarrow 0$ asymptotically for large distances.

If the external field is weak (*i.e.*, small compared with $\frac{e}{r_0^2} \sim \frac{10^{-10}}{10^{-26}} = 10^{16}$ e.s. units), L can be expanded

$$L = \frac{1}{a^2}\left(\sqrt{1 + a^2 \sum_{k>l} (f_{kl}^{(e)} + f'_{kl})^2} - 1\right) = L' + \sum_{k>l} p'_{kl} f_{kl}^{(e)} + \dots \qquad (7.10)$$

Here we have added the constant $-1/a^2$ to L; for, otherwise, L would become infinite as $V/a^2 = Ve^2/r_0^4\, V$ with the volume, and it is reasonable to remove this term.

We now look for an approximate solution of $\delta \int L\, dx_1\, dx_2\, dx_3\, dx_4 = 0$, taking for ϕ'_k the corresponding functions of the uniform motion, but treating the singularity (or the centre) as moving, as that its co-ordinates x_0, y_0, z_0 are functions of t.

A co-ordinate system Σ° can always be so chosen that, for any given value of t, the centre has the velocity zero. For such a system we have the formulæ for the stationary electron derived above; and, on the supposition that f'_{kl} is nearly independent of x, y, z, the integration can be carried out for these variables. Thus

$$\int L\, dx_1^\circ\, dx_2^\circ\, dx_3^\circ\, dx_4^\circ = -4\pi i c \int \Lambda^\circ\, dt^\circ, \qquad (7.11)$$

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† I am indebted to Dr. J. H. C. Thompson for the calculation of this function, and of the other integrals which occur; also for help with the translation from the German.

where, with the notation

$$\mathbf{D}' = -i\,(p'_{14}, p'_{24}, p'_{34}), \quad \mathbf{E}^{(e)} = i\,(f_{14}{}^{(e)}, f_{23}{}^{(e)}, f_{34}{}^{(e)}) = -\left(\frac{\partial \phi^{(e)}}{\partial x}, \frac{\partial \phi^{(e)}}{\partial y}, \frac{\partial \phi^{(e)}}{\partial z}\right),$$

we have

$$4\pi\Lambda^\circ = -\iiint dx^\circ\, dy^\circ\, dz^\circ\, \mathrm{L}' + \iiint dx^\circ\, dy^\circ\, dz^\circ\, \mathbf{D}' \operatorname{grad} \phi^{(2)}. \qquad (7.12)$$

The last integral can be transformed into

$$\iint \phi^{(e)}\, \mathbf{D}'_r\, d\sigma - \iiint \phi^{(e)} \operatorname{div} \mathbf{D}'\, dx^\circ\, dy^\circ\, dz^\circ\,;$$

and, according to (7.3), we have div $\mathbf{D}' = 0$. Let us further suppose that $\phi^{(e)}$ is approximately constant over the extent of the electron (radius r_0), so that the surface integral is, according to (7.4),

$$4\pi\phi^{(e)}\, e.$$

Further

$$\iiint \mathrm{L}'\, dx^\circ\, dy^\circ\, dz^\circ = \frac{4\pi}{a^2}\int_0^\infty \left(\sqrt{1 - a^2\phi'^2} - 1\right) r^2\, dr = -4\pi b_1 \frac{e^2}{r_0}, \qquad (7.13)$$

where

$$b_1 = \int_0^\infty \left(1 - \frac{x^2}{\sqrt{1 + x^4}}\right) x^2\, dx = 0{\cdot}619. \qquad (7.13\text{A})$$

We put the constant (7.13) equal to $-4\pi m_0 c^2$, so that

$$m_0 c^2 = b_1\, e^2/r_0. \qquad (7.14)$$

Thus

$$\Lambda^\circ = m_0 c^2 + e\phi^{(e)}. \qquad (7.15)$$

Let us now change over to an arbitrary co-ordinate system; we have then

$$\int \Lambda^\circ\, dt^\circ = \int \Lambda\, dt = \int \{m_0 c^2 \sqrt{1 - (v^2/c^2)} + (e/c)\,(v_1\phi_1{}^{(e)} + v_2\phi_2{}^{(e)} + v_3\phi_3{}^{(e)} - c\phi_0{}^{(e)})\}\, dt, \qquad (7.16)$$

where $\mathrm{v}\,(v_1, v_2, v_3)$ is the velocity vector of the centre of the electron. This is the known "principle of action"† for the motion of a point electron with rest-mass m_0.

There seems to me no doubt that the next approximation (radiation and its reaction) will give the known results of the classical theory. In higher approximations, however, deviations are to be expected.

Naturally there are solutions for more than one particle at large distances apart. For, if the fields of the particles do not overlap, ϕ can be built up by simple addition. With particles nearer together there is interaction, which can be treated by perturbation methods. It would be important to determine whether, in this case, the usual formulæ will be obtained, and when deviations are to be expected.

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† Born, 'Ann. Physik,' vol. 28, p. 571 (1909).

Our theory allows, however, processes which have no analogy in the old theory, *e.g.*, the complete fusion of two particles. Thus two electrons can fuse into one particle, whose radius is determined by

$$r_1 = \sqrt{a \,.\, 2e} = r_0 \sqrt{2}, \qquad (r_0 = \sqrt{ae}),$$

and whose mass is

$$m_1 = \frac{b_1}{c^2} \frac{(2e)^2}{r_1} = \frac{4r_0}{r_1} m_0 = \sqrt{8m_0}, \qquad \left(m_0 = \frac{b_1}{c^2} \frac{e^2}{r_0}\right).$$

The energy required is thus

$$(m_1 - 2m_0)\, c^2 = 0 \cdot 83\, m_0 c^2 = 432{,}000 \text{ electron-volts},$$

and the structure is highly unstable. I have only given this simple calculation to show how I imagine it possible to deal with the nucleus formation, provided that we had an explanation of the mass of the proton.

In this theory light waves are no independent structure.† There are very weak alternating fields, which somewhere at large distances have an electron as centre of emission. Thus it is to be expected that, also in the quantum theory, photons must be regarded as mathematical constructions rather than as physical realities.

§ 8. *An Attempted Quantization of the New Field-equations.*

The following treatment of a possible quantization process‡ is completely hypothetical, and at present rests only on a formal foundation.

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† Any solution of Maxwell's classical equations for which $\mathbf{E}^2 = \mathbf{H}^2$ (as for a plane or spherical light wave) is also a solution of the new field equations; but the superposition of two waves of this type is not a solution.

‡ For a long time Einstein had advocated the point of view that there must be a non-linear field theory containing the quantum laws. We have here a non-linear field theory, but I do not believe that the quantization can be dispensed with. For the charge is a constant of integration, but is not necessarily a whole number; and also the constants e and h do not occur in the action integral. I believe the following: every theory, built up on classical foundations, requires, for the completion of its assertions, an extension by initial and boundary conditions, satisfying only statistical laws. The quantum theory of the field provides this statistical completion, not, however, in the external manner of the classical theory, but through an inner fusion of the statistical and causal laws.

The " independent integral " is again, exactly as (5.8),

$$S = \int \{p_0\, dx + \sum_{k > l} p_{kl}\, (d\phi_k\, dx^{(l)} - d\phi_l\, dx^{(k)})\}, \tag{8.1}$$

only here the p_{kl} are different from the f_{kl}.

Since the new theory shows complete symmetry in

$$f_0 = L,\ f_{kl} \text{ and } p_0 = -H,\ p_{kl}{}^*, \tag{8.2}$$

it is to be expected that this will also be the case for the quantization. In order to attain this, we must permit only a limited selection for the region of integration in the x_1, x_2, x_3, x_4-space. We imagine curvilinear co-ordinates u_1, u_2, u_3, u_4 introduced ; then, according to Laplace's determinantal law,

$$dx = dx_1\, dx_2\, dx_3\, dx_4 = \frac{\partial\,(x_1\, x_2\, x_3\, x_4)}{\partial\,(u_1\, u_2\, u_3\, u_4)}\, du_1\, du_2\, du_3\, du_4$$

$$= \sum_{k,l} \frac{\partial\,(x_k x_l)}{\partial\,(u_1 u_2)} \cdot \frac{\partial\,(x_k x_l)^*}{\partial\,(u_3 u_4)}\, du_1\, du_2\, du_3\, du_4,$$

where the * again denotes dual quantities, *e.g.*,

$$\frac{\partial\,(x_2 x_3)^*}{\partial\,(u_3 u_4)} = \frac{\partial\,(x_1 x_4)}{\partial\,(u_3 u_4)}.$$

If, now, the sum of these six terms reduces to a single term, we can write

$$d\sigma = \frac{\partial\,(x_k x_l)}{\partial\,(u_1 u_2)}\, du_1\, du_2, \qquad d\sigma' = \frac{\partial\,(x_k x_l)^*}{\partial\,(u_3 u_4)}\, du_3\, du_4, \tag{8.3}$$

and have then

$$dx = d\sigma \,.\, d\sigma', \qquad V = \int dx = \sigma \,.\, \sigma'. \tag{8.4}$$

We admit only such world-regions, whose volume can be expressed as the product of two *dual surfaces*. Thus (8.1) can be written

$$S = \int \{p_0\, d\sigma' \,.\, d\sigma + \sum_{k > l} p_{kl}\, d\sigma' \,.\, f_{lk}\, d\sigma\}.$$

Writing

$$P_0' = \int p_0\, d\sigma', \qquad P'_{kl} = \int p_{kl}\, d\sigma', \qquad F_{kl} = \int f_{kl}\, d\sigma,$$

we have

$$S = \int \{P'_0\, d\sigma + \sum_{k > l} P'_{kl}\, d\,F_{lk}\}.$$

The simplest form of S is the linear form, for which P'_0, P'_{kl} are constants, and

$$S = P'_0\sigma + \sum_{k>l} P'_{kl}F_{lk}. \tag{8.7}$$

If, now, $P'_0 = -H$ is a function of the P'_{kl}, we should have for $\psi = e^{iS}$ the differential equation which is obtained by substituting the operators

$$P'_0 = \frac{1}{i}\frac{\partial}{\partial\sigma}, \qquad P'_{kl} = \frac{1}{i}\frac{\partial}{\partial F_{lk}} \tag{8.8}$$

in

$$P'_0 + H(P'_{23}, \ldots P'_{14}) = P'_0 - \frac{1}{a^2}\sqrt{1 - a^2 \sum_{k>l} P'^2_{kl}}, \tag{8.9}$$

and allowing the resultant operator to act on ψ. In point of fact this does not work, since H is not linear in the p_{kl}, and in no way depends simply on the surface integrals P'_{kl}.

The idea suggests itself that the "wave equation" for ψ must really be linear, in order that the principle of superposition should be satisfied. This can in fact be attained by a formally slight modification, which Dirac has used in his wave theory of the electron.

ψ is regarded as a quantity with more than one component. We introduce certain operators γ_0, γ_{kl} $(= -\gamma_{lk})$, which act on the component suffixes of ψ; and replace the operator (8.9) by the linear

$$a^2\gamma_0 P'_0 + a \sum_{k>l} \gamma_{kl}P'_{lk} - 1. \tag{8.10}$$

The γ_0, γ_{kl} must satisfy certain commutation relations, namely,

$$\gamma_0^2 = 1, \qquad \gamma_0\gamma_{kl} + \gamma_{kl}\gamma_0 = 0, \qquad \gamma_{kl}\gamma_{mn} + \gamma_{mn}\gamma_{kl} = \delta_{km}\delta_{ln}. \tag{8.11}$$

Multiplying (8.10) by the "conjugate" operator

$$a^2\gamma_0 P'_0 + a \sum_{k>l} \gamma_{kl}P'_{lk} + 1,$$

we obtain the operator

$$a^4 P'^2_0 + a^2 \sum_{k>l} P'^2_{kl} - 1,$$

which is equivalent to the square of (8.9).

I should like to suggest that (8.10), acting as a common differential operator on a function ψ of the surface area σ, and of the surface integrals of the field components F_{kl} (but for arbitrary choice of the integration surfaces), contains the quantum laws of the field. But I cannot prove this hypothesis by its consequences, and I have only one physical consideration which seems to confirm the assumption that the surface integrals of the field components are the real quantum variables of the field.

Let us consider a static (non-radiating) field, and introduce polar co-ordinates r, α, β. The spheres $r =$ constant (variables α, β) are clearly dual to the cylinders (variables r, t). The integrals F_r and $\mathrm{P}'_r = \int p_r d\sigma' = 4\pi r^2 p_r$ are therefore conjugate. The latter represents the charge e of the system, which in the classical treatment is an integration constant. Thus, in quantum theory, ψ will have the factor

$$e^{ie}\mathrm{F}_r. \tag{8.10}$$

If we suppose that the range of values of f_r in the world-region considered is finite, and thus also that of F_r, it follows that

$$e = 2\pi n \qquad (n \text{ a whole number}). \tag{8.11}$$

Our quantum law means that, in a region of space where the field strength is within finite limits, the charge must be an integral multiple of a charge element, which, through our choice of units, has the value unity.

The usual quantum mechanics is the limiting case in which the self-field is regarded as rigidly bound to the centre. The field quantities become, then, only functions of the motions of the centres of the particles. Whether and how this limiting case (including Pauli's exclusion principle) comes out of the hypothetical formulæ (8.10), I cannot yet say ; nor can I say how the other limiting case of light may be dealt with. Also I do not know whether the introduction of the γ-quantities gives the spin of the particles correctly, nor whether the existence of two different masses can be established by means of this theory.

On the Absorption Spectra of the Sulphides of Zinc, Cadmium, and Mercury from λ 7000–1900, and the Heat of Dissociation of Sulphur.

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(Communicated by M. N. Saha, F.R.S.—Received August 9, 1933.)

Introduction.

The sulphides of zinc, cadmium, and mercury form part of the following series of diatomic compounds :—

ZnO	CdO	HgO
ZnS	CdS	HgS
ZnSe	CdSe	HgSe
ZnTe	CdTe	HgTe

which are all chemically similar. One of the constituents of these substances has a positive and the other a negative electrovalency of two :—

positive electrovalency of two—Zn, Cd, Hg.
negative electrovalency of two—O, S, Se, Te.

In a previous paper[*] the absorption spectra of ZnO and CdO were investigated by the present author. It was found that the vapours of these compounds absorb light continuously from a long wave limit—a phenomenon in which these resemble the alkali halides,[†] first investigated by Franck and his co-workers and continued by others.

For explaining the absorption spectra of these compounds it was postulated that in the vapour state the binding is ionic in nature, being of the form $Zn^{++}O^{--}$. This hypothesis was further corroborated by calculating the energy of binding according to a Born cycle and comparing the calculated value with the position of the observed beginning of absorption. Fair agreement was found for ZnO and CdO. After this work was finished it was thought advisable to extend the same investigations to other similarly constituted compounds as mentioned above. Before describing these experiments I wish to add a brief discussion on the transition from the ionic to the atomic state of binding in such compounds.

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[*] 'Bull. Acad. Sci., U.P., Allahabad,' vol. 2, p. 245 (1933).

[†] Franck, Kuhn, and Rollefson, 'Z. Physik,' vol. 43, p. 155 (1927).

The ideal state of binding is one in which both components can be regarded as spherically symmetrical ions just touching each other as in Na^+Cl^-. But such a state is only ideal as, owing to strong forces of electrostatic attraction, both the ions are deformed. Na^+ will be only slightly deformed as each of the six $2p$-electrons forming the outer shell of Na^+ is very strongly attached to the nucleus. (The ionization potential of Na^+, *i.e.*, the energy required to tear off one $2p$-electron from Na^+ is 47 electron volts.) But in the presence of Na^+, Cl^- will be rather strongly deformed, as the field of Na^+ is large, and very little force is necessary to deform the Cl^- electron. (The electron affinity of Cl^- is only 4 volts.)

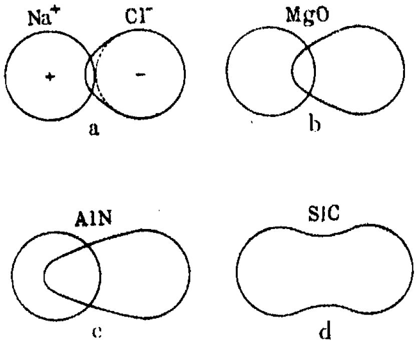

FIG. 1.—After Fajans. "The George Fisher Non-Resident Lectureship at Cornell University, 1931" (McGraw Hill).

But if we take MgO, then supposing that the constitution is $Mg^{++}O^{--}$, we find that though Mg^{++} will not be at all deformed, O^{--} will be very strongly deformed as it can easily lose two extra electrons and the deforming force due to Mg^{++} is much stronger than that due to Na^+. Hence, in MgO the deformed O^{--} will behave as in fig. 1, *b*; that is, the departure from the ionic binding will be more prominent. This tendency will be more pronounced as we take AlN and SiC, and in the latter binding is presumably completely atomic and due to forces of the Heitler-London type. This gradual transition from the ionic type of binding to the atomic can be followed if we study successively the absorption spectra of a series like NaCl, MgO, AlN, and SiC. But such investigations are difficult to carry out owing to the high temperatures at which some of these compounds sublime; for some this is above 2000° C. The graphite furnace is capable of attaining a temperature of 2500° C. But above 2000° C. it is not possible to carry out absorption experiments satisfactorily as owing to high temperature the beginning of absorption is enormously shifted.

Fajans* first pointed out (which was confirmed by Grimm†) that the deformation—that is to say, the departure from the spherical ionic type—becomes more prominent as the charge of the positive ion increases. The structure of ZnO was postulated to be $Zn^{++}O^{--}$, and the structure of Zn^{++} is $3d^{10}$. If Fajans' ideas be correct, the deformation of O^{--} ion produced by Zn^{++} will be appreciable and ZnO will be more atomic than compounds like CuCl or AgCl. A knowledge of the band spectra of these compounds is sure to throw much light on the subject.

In Paper I (*loc. cit.*) it has been shown that for $Zn^{++}O^{--}$ gas, say, when light is allowed to pass through the vapour, both the electrons from O^{--} are simultaneously transferred to Zn^{++} and two normal atoms are obtained. That is, the process of photochemical dissociation is

$$\mathrm{ZnO} + h\nu_1 = \mathrm{Zn} + \mathrm{O}\,(^3\mathrm{P}).$$

We may try to visualize the interaction of light with ZnO-vapour with the aid of a Franck-Condon‡ diagram. The normal state n_1 is represented by a curve with a deep minimum and the upper state by a sloping curve α. By an electronic transition the compound is raised from A to B vertically with the absorption of a quantum $h\nu_1$ of light; a simultaneous dissociation occurs since B lies above the dissociation continuum of α. As the dissociation continuum of n_1 lies far above that of α these two curves intersect.

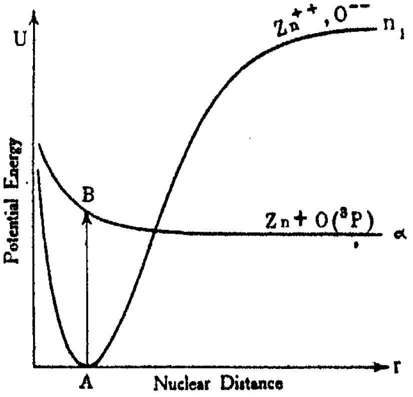

Fig. 2.

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[*] 'Z. Kristallog.,' vol. 66, p. 321 (1925).

[†] 'Z. Elektrochem.,' vol. 34, p. 502 (1928).

[‡] Condon, 'Phys. Rev.,' vol. 28, p. 1182 (1926); vol. 32, p. 858 (1928).

As mentioned in the previous work, a good confirmation that α represents two normal atoms would be supplied if we could establish from experimental data two more curves for the excited molecule consisting of a normal Zn atom with the oxygen atom in the states $^1D_2$ and $^1S_0$. In such cases the absorption spectrum would consist of the first cut as mentioned above (indicative of the photo-dissociation of ZnO into Zn and normal O(^{3}P)) then a retransmission patch followed by a second absorption cut which indicates the decomposition of ZnO into Zn and O excited to $^1D_2$ state. This will again be followed by a retransmission patch indicative of the dissociation of ZnO into Zn and O excited to $^1S_0$ state. The frequency difference between the different initial cuts will be ^3P—$^1D_2$ and $^1D_2$—$^1S_0$ of oxygen approximately. The same will hold for the other compounds. For ZnO and CdO calculation showed that the second and third cuts fall within the fluorite region which is beyond the capacity of the apparatus of this laboratory. Hence, only the absorption due to normal state of oxygen could be found in these cases.

Since the absorption spectra of the corresponding sulphides are expected to be similar to the oxides, a preliminary thermochemical calculation was carried out to find out whether the absorptions which can be ascribed to the normal, and the metastable states $^1D_2$ and $^1S_0$ would fall within the quartz region. The present work was undertaken in order to try to find these states and to obtain experimental confirmation of the above ideas. We can represent the expected processes for all the three absorption cuts as follow :—

$$\mathrm{ZnS} + h\nu_1 = \mathrm{Zn} + \mathrm{S}\ (^3\mathrm{P})$$
$$\mathrm{ZnS} + h\nu_2 = \mathrm{Zn} + \mathrm{S}\ (^1\mathrm{D}_2)$$
$$\mathrm{ZnS} + h\nu_3 = \mathrm{Zn} + \mathrm{S}\ (^1\mathrm{S}_0).$$

Experiment.

Of the three compounds the vapour pressure of only HgS is known. And in standard chemical treatises we get a bare idea of the sublimation points of ZnS and CdS. As usual, the well-known graphite furnance* of our laboratory was brought into use. Unlike other furnaces this furnace takes up the desired temperature very quickly—a condition so often necessary when the vapour of the substances diffuse quickly as in the present experiments. To prevent distillation as well as to avoid the wear and tear of the graphite tubes through oxidation the absorption chamber was filled with nitrogen which did not combine with any of the substances investigated. The source of continuous spectrum was a hydrogen discharge tube run by a 2 kW. transformer for the visible, violet, and ultra-violet regions, and a pointolite lamp for the visible, red, and infra-red. For the violet and ultra-violet regions both the E_2 and E_3 quartz spectrographs were employed, and a constant deviation spectrograph was used for the visible, red, and infra-red regions. The copper arc served for comparison, and it was replaced by a Neon lamp when investigations were taken up in the red and infra-red. Schumann, process and panchromatic plates were used for the respective regions.

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* Desai, 'Proc. Roy. Soc.,' A, vol. 136, p. 76 (1932).

All the sulphides evolve sulphur at high temperatures. To avoid this decomposition the temperatures were kept as low as possible, though high enough to give sufficient vapour for absorption, but with some substances it was found impossible to avoid sulphur bands. The substances were introduced into the furnace in quartz tubes when temperatures above 500° C. were used, and in Pyrex glass tubes for lower temperatures. For ZnS a temperature of the order of 800°–850° C., for CdS 750°–800° C., and for HgS 450°–550° C. was found quite suitable.

To locate definitely the beginning of absorption, microphotometric records of the plates were taken at Aligarh. For each substance the spot was allowed to run along the absorption spectrum and then along the continuous spectra. The magnification used was 1 : 2. I am very grateful to Dr. R. K. Asundi, Reader in Physics, the Muslim University, Aligarh, for taking the microphotograms for me, and also to Professor Samuel and other authorities of the Muslim University, Aligarh, for kindly allowing me the use of their apparatus.

Results.

ZnS.—At temperatures higher than 900° C. the presence of S_2 absorption bands of Christy and Naude* indicated dissociation of ZnS. It was found that the group belonging to the $0 \leftarrow n$ transition appeared strongly on the plates. The extreme ultra-violet bands were not obtained, probably owing to the high temperature as Christy and Naude (*loc. cit.*) have mentioned. On varying the temperature conditions the bands disappeared and continuous absorption apparently beginning from λ 2800 appeared as shown by the enclosed microphotogram. There was also a transmitted patch of light with a second absorption beginning from λ 2150 nearly. The resonance line λ 2136 of zinc came in absorption showing that there were some free zinc atoms due to decomposition.

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* 'Phys. Rev.,' vol. 37, p. 903 (1931).

But the number of free zinc atoms was small since the line was quite narrow.

CdS.—At 500°–600° C. nothing of absorption was seen except the resonance line λ 2288 of cadmium due to slight decomposition of CdS similar to ZnS. But at about 750°–800° C. there was a continuous absorption beginning from λ 3150. The retransmission of light was obtained in this case, too, with a second absorption cut beginning from λ 2350. In this condition the λ 2288 line was slightly broadened, evidently due to the formation of Cd_2 molecule as postulated by Winans* and the absorption of the intercombination line λ 3261 was also noticeable. One can infer from the result that the temperature was comparatively high.

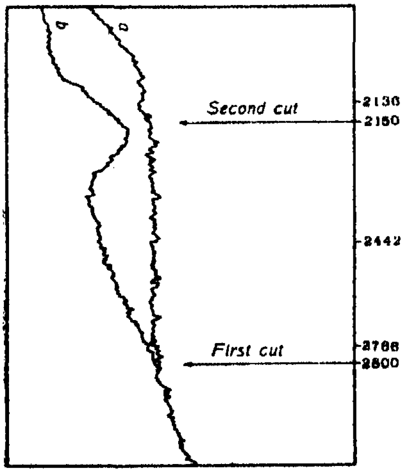

Fig. 3.—(*a*) Microphotograph of the continuous spectrum; (*b*) microphotograph of the absorption spectrum of ZnS.

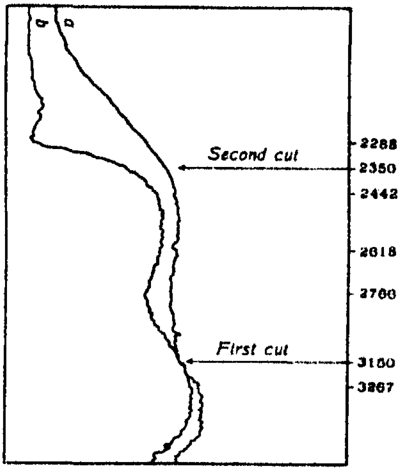

Fig. 4.—(*a*) Microphotograph of the continuous spectrum; (*b*) microphotograph of the absorption spectrum of CdS.

HgS.—With mercuric sulphide the thermal decomposition was present in all stages to a fair extent, and sulphur bands could never be avoided. At lower temperatures of the order of 300° C., some fresh bands appeared from λ 3800 to λ 2300 which were quite different in appearance to those of S_2 given by Christy and Naude (*loc. cit.*). The absorption by the sulphide was not at all prominent at this stage, and the resonance line λ 2536 of mercury was clearly visible indicating thermal decomposition of HgS. By performing a separate absorption experiment with pure sulphur in the absorption chamber under the same condition it was found that the foregoing bands appeared again. These bands are probably due to S_4,* according to Henri S_6 or S_8, as according to Preunner and Schupp† and others, sulphur exists in these states at temperatures lower than 500° C., while above 500° C. the sulphur molecule has the constitution S_2. As the temperature was raised to 500° C. and above a good quantity of the vapour of HgS was obtained and the absorption by the sulphide was superposed on the absorption bands of sulphur, some of which disappeared at these temperatures. At the same time S_2 bands came in view from about λ 3500 to λ 3200 where the absorption by the sulphide was not present, the others being superposed by the continuous absorption. The resonance line λ 2536 of mercury lying within the third absorption of HgS was no longer visible. For HgS, therefore, there were in all three regions of continuous absorptions beginning from about λ 4450, λ 3100, and λ 2250 respectively. There were retransmitted patches after either of the first two absorption cuts. It was not possible to obtain all the three cuts simultaneously on the same plate. It has been found that with large exposures the absorption is sometimes superposed on the transmitted light. That is what occurred here. The exposures were increased five-fold to obtain the third patch of retransmitted light which finally did appear faintly but at the cost of the first absorption. With very high vapour pressures also the third patch was not visible.

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* 'Phil. Mag.,' vol. 7, p. 555 (1929).

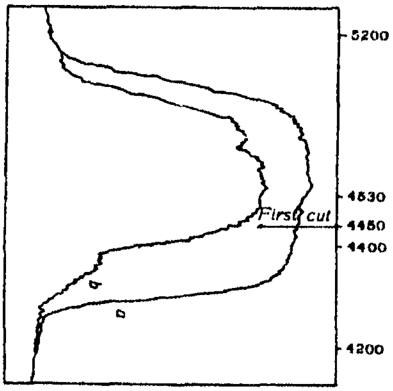

Fig. 5.

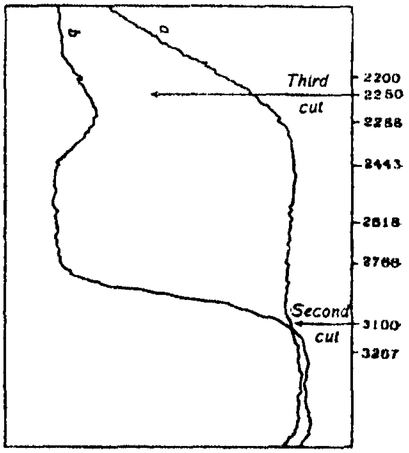

Fig. 6.

Figs. 5 and 6.—(a) Microphotograph of the continuous spectrum; (b) microphotograph of the absorption spectrum of HgS.

Table I gives a list of different beginnings of absorption from long wave limits.

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* Debye, "Molecular Structure," p. 138 (1932).

† 'Z. phys. Chem.,' vol. 68, p. 147 (1909).

Table I.

MS.	1st absorption.	2nd absorption.	3rd absorption.
ZnS	λ 2800	λ 2150	(Beyond the range of quartz)
CdS	λ 3150	λ 2350	,, ,,
HgS	λ 4450	λ 3100	λ 2250

Theoretical Discussion.

Taking R as the heat of dissociation of MS (where M is the metal constituent) into normal M and S, the value of R is given by

$$R = Nh\nu_1/J,$$

where $h\nu_1$ is the beginning of absorption ; and also from a Born cycle

$$R = Q + \tfrac{1}{2}D_{S_2} + L_S + L_M - L_{MS},$$

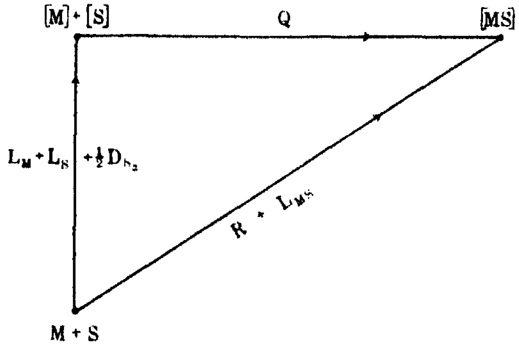

FIG. 7.

where

L_{MS} = latent heat of sublimation of solid [MS].

Q = heat of formation of solid [MS] out of solid [M] and solid $[S]_{\text{rhom}}$.

D_S = heat of dissociation of sulphur S_2 into S atoms

L_M = latent heat of sublimation of [M]

L_S = latent heat of sublimation of solid $[S]_{\text{rhom}}$ to S_2 gas.

Now it is known that*

$$2\,[S]_{\text{rhom}} = (S_2) - 29\cdot 3 \text{ k. cal.},$$

so that

$$L_S = 14\cdot 65 \text{ k. cal.},$$

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* Britzke and Kuputinsky, 'Z. anorg. Chem.,' vol. 194, p. 349 (1930).

and also from Budde's* chemical determination and the determination of Christy and Naudé (*loc. cit.*) from predissociation of S_2, the heat of dissociation of S_2 into atomic sulphur, that is,

$$D_{S_2} = 102\cdot6 \text{ k. cal. nearly.}$$

In Table II the different data and the calculated values of R are given. Most of the data have been taken from Landolt-Börnstein tables (1931).

Table II.

MS.	Q k. cal.	L_M k. cal.	L_S k. cal.	$\frac{1}{2}D_{S_2}$ k. cal.	L_{MS} k. cal.	R k. cal. (calculated).
ZnS	43·0	28·5	14·65	51·3	—	137·5 — L_{ZnS}
CdS	34·0	26·0	14·65	51·3	—	126·0 — L_{CdS}
HgS	10·6	13·9	14·65	51·3	26·4 (calculated from vapour pressure data)	64·0

The values of $R + L_{MS}$ for ZnS and CdS quoted by Grimm† are 145 and 131 k. cal. respectively and differ from mine. This is probably due to the fact that the values of the different quantities in the relation for R were taken from older tables of constants.

Since the latent heats of sublimation of ZnS and CdS are unknown a rough estimate had to be formed from their boiling points with the help of Trouton's rule. But the values for boiling points, viz., 1000° C. for ZnS and 980° C. for CdS, are only approximate.

Trouton's rule states that $L_{MS}/T = C$ (a constant) where T is the boiling point in absolute temperature. The value of C has been determined from that of HgS—

$$C = \frac{L_{HgS}}{T} = \frac{26400}{580 + 273} = 31 \text{ nearly.}$$

Then

$$L_{ZnS} = 1273 \times 31 = 39\cdot5 \text{ k. cal.}$$

and

$$L_{CdS} = 1153 \times 31 = 35\cdot7 \text{ k. cal.}$$

Therefore,

$$R_{ZnS} = 137\cdot5 - 39\cdot5 = 98\cdot0 \text{ k. cal.}$$

$$R_{CdS} = 126\cdot0 - 35\cdot7 = 90\cdot3 \text{ k. cal.}$$

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* Budde, 'Z. anal. Chem.,' vol. 78, p. 169 (1912).

† Grimm, 'Handbuch der Physik,' vol. 24, p. 538 (1927).

The value of R can also be calculated by calculating the lattice energy of crystals. But the necessary data are known only for ZnS.

Let

E = lattice energy of ZnS taking Zn^{++} and S^{--} as units,

$E_{S^{--}}$ = heat of formation* of an S^{--}-ion out of S and two electrons,

$I_{Zn^{++}}$ = sum of the ionization potentials of Zn and Zn^{+}.

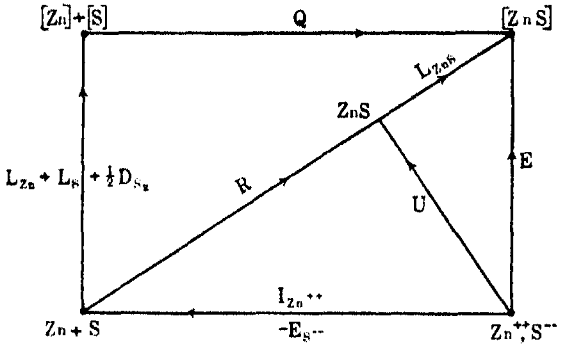

FIG. 8.—Born cycle for ZnS.

Now the value of E given by Born and Gerlach† is 740 k. cal. It has been calculated in the following way :—

$$E = 2690 \,.\, \frac{n-1}{n} \,.\, \sqrt[3]{\frac{\rho}{M}} \,,$$

where ρ is the density, M the molecular weight and n the repulsion exponent

$$n = 1 + 8 \cdot 00 \,.\, 10^{-14} \,.\, \frac{1}{\chi}\left(\frac{M}{\rho}\right)^{4/3} ,$$

where χ is the compressibility.

For ZnS,

$$\chi = 1 \cdot 44 \,.\, 10^{-12},$$

therefore

$$n = 4 \cdot 92,$$

therefore

$$E = 740 \text{ k. cal.}$$

Therefore, from the cycle,

$$\begin{aligned} R + L_{ZnS} &= E - I_{Zn^{++}} + E_{S^{--}} \\ &= 740 - 628 + 30 \\ &= 142 \cdot 0 \text{ k. cal.} \end{aligned}$$

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* Samuel and Lorentz, 'Z. Physik,' vol. 59, p. 59 (1930).

† 'Z. Physik,' vol. 5, p. 443 (1921).

We see that this value is almost the same as that obtained from the other half of the Born cycle. If we suppose that the units are Zn^+ and S^- instead of Zn^{++} and S^{--}, then E will be equal to 740/4; that is, 185 k. cal.

Now I_{Zn^+}, the ionization potential of Zn, $= 215 \cdot 5$ k. cal. and, as quoted by Samuel and Lorentz (*loc. cit.*)

$$E_{S^-} = S + e - 149 \cdot 5 \text{ k. cal.}$$

therefore

$$R + L_{ZnS} = 185 \cdot 0 - 215 \cdot 5 - 149 \cdot 5$$

$$= 119 \cdot 0 \text{ k. cal.}$$

This value is too low and cannot be admitted.

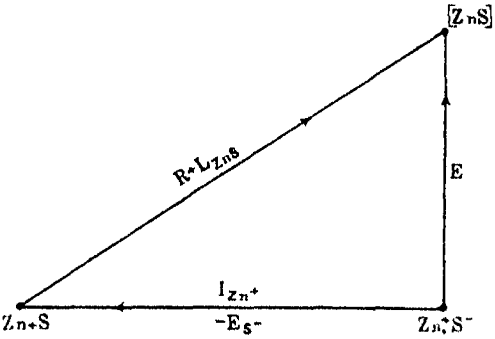

FIG. 9.

Interpretation of Results.

In Table III the values of the different beginnings of absorption as obtained in the present investigation are compared with the corresponding calculated values.

Table III.

MS.	1st absorption.	2nd absorption.	3rd absorption.	R (calculated).
	k. cal.	k. cal.	k. cal.	k. cal.
ZnS	102·1	133·0	(beyond range)	98·0
CdS	90·8	121·7	,,	90·3
HgS	64·2	92·3	127·1	64·0

From the second and last columns it is seen that R corresponds to the first beginning of absorption; that is, to $h\nu_1$ in

$$MS + h\nu_1 = M + S\,(^3P).$$

The next two are, therefore, due to $h\nu_2$ and $h\nu_3$ respectively in

$$MS + h\nu_2 = M + S\,(^1D_2),$$
$$MS + h\nu_3 = M + S\,(^1S_0).$$

Therefore, $h\nu_1 - h\nu_2$ ought to give the difference between ^3P and $^1D_2$ terms of sulphur, and $h\nu_2 - h\nu_3$ that of $^1D_2 - {}^1S_0$. The experimental values have been given in Table IV.

Table IV.

MS.	$h\nu_1 - h\nu_2 = {}^3P - {}^1D_2$ of S.	$h\nu_2 - h\nu_3 = {}^1D_2 - {}^1S_0$ of S.
ZnS	30·9 k. cal. = 1·34 volts	—
CdS	30·9 k. cal. = 1·34 volts	—
HgS	28·1 k. cal. = 1·22 volts	34·8 k. cal. = 1·51 volts

These values of $^3P - {}^1D_2$ and $^1D_2 - {}^1S_0$ can only be approximate, as is clear from the nature of the transitions as explained on p. 450. Let us see whether these values are confirmed by our present knowledge of atomic spectrum.

Arc Spectrum of Sulphur.—The arc spectrum of sulphur is yet only imperfectly studied. The latest work is that of Frerichs* who has studied the triplet system and has obtained the absolute values of terms from a number of Rydberg sequences. The singlet $^1D_2$ and $^1S_0$ terms have not yet been obtained, but Christy and Naudé (*loc. cit.*), from a study of the predissociation spectra of S_2, have given the value for $^3P - {}^1D_2$ to be 1·6 volts. It was shown that the main system of S_2 bands, like the Schumann-Runge bands of oxygen, is due to a transition $^3\Sigma^-_u \leftarrow {}^3\Sigma^-_g$ and it was postulated that the $^3\Sigma^-_g$ state arises from two S atoms in the ^3P state, while $^3\Sigma^-_u$ arises from a molecule in which the constituents are ^3P and $^1D_2$. The convergence limit of $^3\Sigma^-_u$ was extrapolated from a $\omega(v) : v$ curve and the energy of dissociation of $^3\Sigma^-_g$ state was obtained as 4·45 volts from the diffusivity of the S_2 bands. Thus the difference $^3P - {}^1D_2$ comes out to be $6{\cdot}05 - 4{\cdot}45 = 1{\cdot}6$ volts. This value is most probably high since according to experience such extended extrapolation lead generally to high values. But according to Christy and Naudé the value 1·6 volts for $^3P - {}^1D_2$ of S is said to be in good agreement with that obtained from an interpolation of Frerichs'† value of 1·95 volts for oxygen, and the values 1·3 and 1·2 volts respectively for Se and Te given by McLennan and Crawford.* This interpolation cannot be expected to be correct since McLennan and Crawford's results for the oxygen group have been superseded, and the recent values are for $^3P - {}^1D_2$ of Se† 0·87 volts, and for Te‡ 0·72 volts. Interpolating again with the later values of $^3P - {}^1D_2$ for Se and Te with that of oxygen, we get 1·45 volts nearly for sulphur. In the present experiment $^3P - {}^1D_2$ has come out at 1·3 volts nearly, and agrees better with the value 1·45 volts as obtained above.

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* 'Z. Physik,' vol. 80, p. 150 (1933).

† 'Phys. Rev.,' vol. 36, p. 398 (1930).

The value given for $^1D_2 - {}^1S_0$ of S equal to 1·51 volts in Table IV is new, and as yet there are no other experimental data about this difference. From the arc spectrum of sulphur this value is expected to lie between 2·1 volts (for oxygen) and 1·7 volts (for selenium).

Conclusion.

In fig. 10, the different states of ZnS have been represented by means of potential energy curves. Here only two more states β and γ have been added to those of fig. 2 to represent the interaction of Zn atom with S ($^1D_2$) and S ($^1S_0$) respectively. From the results and calculations it is seen that the ideas expressed for ZnO and CdO, that these compounds are ionic in nature in the gaseous state, are applicable also to sulphides. The position of the dis-

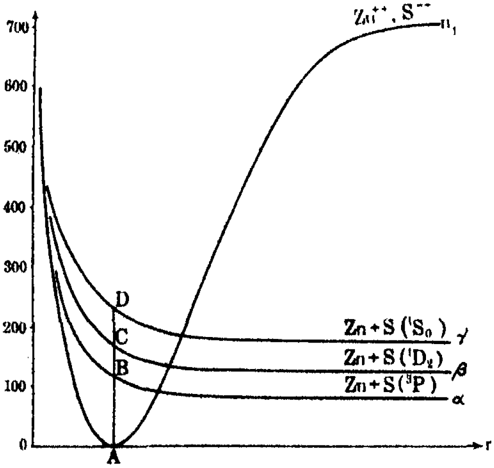

FIG. 10.

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* 'Nature,' vol. 124, p. 874 (1929).

† Gibbs and Ruedy, 'Phys. Rev.,' vol. 40, p. 204 (1932).

‡ Ruedy and White, 'Phys. Rev.,' vol. 41, p. 593 (1932).

sociation continuum of the ground state n_1 representing two free Zn^{++} and S^{--} ions is reached by following up the vibrational levels. But this position is given by $E - L_{ZnS} = U$, fig. 8; that is, 700 k. cal. nearly from a Born cycle. The positions B, C, D giving the different long wave limits of absorption all lie below 700 k. cal., so that the ZnS vapour has no chance of reaching the convergence limit of n_1, as by absorption of light it comes first to the states α, β, and γ. These transitions are electronic and brought about by the simultaneous transition of two electrons from S^{--} to Zn^{++} under the influence of light. The γ-curve for ZnS and CdS would lie beyond the region of a quartz spectrograph, and cannot be investigated with the present equipment of the laboratory.

The experimental values of $^3P - {}^1D_2$ and $^1D_2 - {}^1S_0$ of sulphur are given by the energy values BC and CD, if we assume according to the Franck-Condon principle (*loc. cit.*) that the most probable transition occurs when there is no change in the nuclear distance and in linear momentum. The exact values obtained from arc spectra would correspond to the asymptotic differences of α, β, and γ. Since the exact forms of the upper curves are unknown except that they are slightly sloping, BC and CD cannot be said to be exactly equal to the corresponding difference between the asymptotes. Consequently BC and CD cannot be expected to give correct values of $^3P - {}^1D_2$ and $^1D_2 - {}^1S_0$ of sulphur. With the higher oxides,* the experimental value of $^3P - {}^1D_2$ of oxygen always came lower than that obtained from atomic spectra.

Chances of Single Electron Transition.

The foregoing phenomena all arise out of a simultaneous transition of two electrons from S^{--} to the M^{++} part, but there is a likelihood of obtaining a transition of a single electron as a first step. Here one gets the resulting product out of this photochemical action as M^+S^-.

$$M^{++}S^{--} + h\nu = M^+S^-.$$

Here the electrostatic force is not completely broken and the potential curve still possesses a minimum. To calculate the position of the dissociation continuum of this curve we use the Born cycle (fig. 11), where

$$I_{Zn^+} = \text{ionization potential of Zn}$$
$$E_{S^-} = S + e - 149\cdot5 \text{ k. cal.}$$
$$E_{S^{--}} = S + 2e - 30 \text{ k. cal.}$$

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* Dutta and Sen-Gupta, 'Proc. Roy. Soc.,' A, vol. 139, p. 397 (1933).

therefore

$$E_{S^{--}} = E_{S^-} + e + 119{\cdot}5 \text{ k. cal.}$$

and we get

$$E_2 = 740 - 410 - 119{\cdot}5 - 39{\cdot}5$$
$$= 171{\cdot}0 \text{ k. cal.}$$

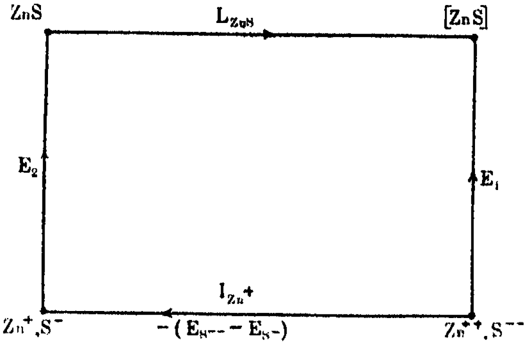

FIG. 11.

Since no bands due to transition $Zn^{++}S^{--} \rightarrow Zn^+S^-$ were obtained in the region λ 7000 to λ 1900, the minimum of the curve n_2 in fig. 12 might be lying very near to that of n_1. At least the dissociation continuum of n_2 lies 171 k. cal. above the minimum of the ground state n_1. The infra-red region is being investigated for the bands.

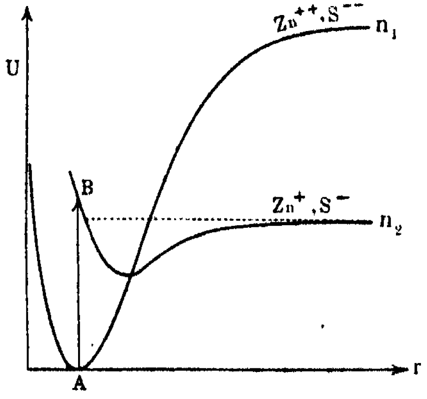

FIG. 12.

There is another possibility. When $Zn^{++}S^{--}$ changes to Zn^+S^- by light absorption the bond is considerably weakened which is evident from the energies required to reach the respective convergence limits. As a result of this weakening the equilibrium nuclear distance may increase considerably, so that the minimum is shifted to the right as shown in fig. 12. A transition

AB, therefore, will give bands in the quartz region, but these were not obtained in the present experiments. Or, if the point B lies above the continuum of n_2, a transition AB by the absorption of light will cause dissociation, the continuous absorption corresponding to which will lie more than 171 k. cal. farther; that is, in the fluorite region of ZnS. This cannot be demonstrated experimentally.

Heat of Dissociation of S_2 *into* S *atoms.*

From the first beginning of absorption it is possible to determine the heat of dissociation of sulphur in the S_2 state to S atoms indirectly. All the data are known only for HgS.

$$R_{(obs.)} = Q + \tfrac{1}{2}D_{S_2} + L_S + L_{Hg} - L_{HgS}$$

i.e.,

$$64 \cdot 2 = 10 \cdot 6 + \tfrac{1}{2}D_{S_2} + 14 \cdot 65 + 13 \cdot 88 - 26 \cdot 4,$$

therefore

$$D_{S_2} = 102 \cdot 9 \text{ k. cal.}$$

This value agrees very well with the values of heat of dissociation determined by Budde (*loc. cit.*) chemically, and by Christy and Naudé (*loc. cit.*) from predissociation of S_2.

[*Note added in proof, October* 22, 1933.—Recently Ruedy ('Phys. Rev.,' vol. 43, p. 1045 (A), (1933)) has reported the discovery of the singlet term of the arc spectrum of sulphur and has given the term values as follows :—

$$^1D_2 - 74315 \text{ cm.}^{-1}$$

$$^1S_0 - 64522 \text{ cm.}^{-1}$$

With Frerichs' (*loc. cit.*) already known values of $^3P_{2,1,0}$ terms the following term differences are obtained.

$$^3P_2 - {}^1D_2 = 83554 - 74315 = 9239 \text{ cm.}^{-1} = 1 \cdot 41 \text{ volts.}$$

$$^1D_2 - {}^1S_0 = 74315 - 64522 = 9793 \text{ cm.}^{-1} = 1 \cdot 21 \text{ volts.}$$

My results for $^3P - {}^1D_2$ given in this paper are only slightly at variance with these values. The value of $^1S_0$ requires further confirmation.]

In conclusion, the author wishes to express his sincerest thanks to Professor M. N. Saha, D.Sc., F.R.S., for the valuable guidance rendered during the course of the work.

Summary.

(1) The absorption spectra of the sulphides of zinc, cadmium, and mercury have been studied in the region λ 7000 to λ 1900. The vapours of these substances absorb light continuously from a long wave limit resulting in photochemical dissociation into two normal atoms, in accordance with the following photochemical equation—

$$MS + h\nu_1 = M + S\,(^3P).$$

After the first absorption there is a retransmitted patch and a second absorption corresponding to

$$MS + h\nu_2 = M + S\,(^1D_2).$$

For HgS there is another retransmitted patch of light with a third absorption corresponding to

$$MS + h\nu_3 = M + S\,(^1S_0).$$

(2) The differences $h\nu_1 - h\nu_2 = 1{\cdot}3$ volts and $h\nu_2 - h\nu_3 = 1{\cdot}51$ volts are attributed to the values of $^3P - {}^1D_2$ and $^1D_2 - {}^1S_0$ of sulphur respectively.

(3) It is postulated that the compound MS is ionic in nature, of the type $M^{++}S^{--}$ in the gaseous state. With the passage of light both the electrons from S^{--} are simultaneously transferred to M^{++} giving two normal atoms, the linkage being broken.

(4) The possibility of the formation of $Zn^{+}S^{-}$ out of the transition of a single electron from S^{--} to Zn^{++} in $Zn^{++}S^{--}$ has been discussed.

(5) Heat of dissociation of S_2 into S atoms has been indirectly determined to be 102·9 k. cal.

The Mechanical Moment of the Nucleus of Cæsium.

By D. A. Jackson, Clarendon Laboratory, Oxford.

(Communicated by F. A. Lindemann, F.R.S.—Received August 23, 1933.)

Introduction.

In an earlier work,* from measurements on the separations of the hyperfine structure doublets of the lines of the principal series, the author was able to find an approximate value for the magnetic moment of the nucleus of cæsium; but from these measurements it was not possible to determine experimentally the mechanical moment. In order to determine this, it is necessary to know accurately the intensity ratios of the components of the doublets. Accordingly accurate intensity measurements were made on the two most suitable doublets, 4555 and 4593. By working with extremely low vapour pressures of cæsium in the light source, the effect of self-absorption on the intensity ratios was almost entirely eliminated, being reduced to less than 2% in the stronger doublet and 1% in the weaker doublet. When this small correction was applied, the intensity ratio was found to be $1\cdot27 \pm 0\cdot02$ for both doublets. This establishes with certainty the value 7/2 for the mechanical moment of the cæsium nucleus.

Excitation of the Spectrum.—The light source used was an external electrode discharge tube, the ends of which were 6 cm. long and 5 cm. in diameter; the capillary was 4 cm. long and 5 mm. bore. The tube was made of pyrex glass, carefully "baked out" in a very high vacuum; after this a small quantity of pure cæsium was distilled into it. The metal was distilled three times before it entered the discharge tube in order to eliminate as far as possible traces of occluded hydrogen, which are always present in alkali metals. After the introduction of the metal, the tube was filled with neon, purified by charcoal cooled with liquid air, at a pressure of 2 mm. of mercury. External electrodes made of thin annealed sheet copper, and large enough to cover the whole of the ends of the tube, were fitted. In order to excite the tube, one of the external electrodes was connected to one end of the plate coil of a high frequency oscillator of the type described by Gutton†; the other electrode was earthed. The oscillator was capable of an output of about ½ kw., and was excited by a generator giving currents up to 5 amps. at a potential of 1750 volts.

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* 'Proc. Roy. Soc.,' A, vol. 121, p. 432 (1928).

† 'Onde Electrique,' vol. 4, p. 387 (1925).

The discharge tube was run in a vertical position; the lower end being immersed in a bath of pure paraffin of high boiling point. Since the cæsium present in the tube was in the lower end, and the capillary while the discharge was taking place was heated to a higher temperature than the lower end (rendering condensation of the metal impossible) the pressure of cæsium in the capillary was equal to the vapour pressure of the metal at the temperature of the paraffin bath. By varying the temperature of the bath it was possible to obtain the lines of the cæsium spectrum emitted from cæsium vapour at accurately known pressures.

Examination of Structure of the Lines.—The hyperfine structure of the lines 4555 and 4593 of cæsium was examined with a glass Lummer Gehrcke plate of thickness 4·716 mm. and length 13 cm. and refractive index, μ_D, 1·50911, made by Hilger. The auxiliary dispersion was a Hilger E_2 spectrograph, and a quartz-fluorite achromat of 35 cm. focus was used to focus the interference fringes of the Lummer Gehrcke plate on to the spectrograph slit. The Lummer Gehrcke plate was of very high quality, being entirely free from ghosts and possessing its full theoretical resolving power. The length of the plate is such that there are 17 reflexions, and consequently 17 interfering beams of light; and the thickness of a line in the image of the fringes was found to be about 1/15 of the distance between two successive orders. If the slight diminution in intensity of each successive beam of light is taken into consideration, it is apparent that the resolving power is not sensibly less than the theoretical. The Lummer Gehrcke plate was fitted with a Twyman prism, so that the whole optical system lay in a plane. The light emitted by the capillary of the discharge tube was focussed by a condensing lens of 5 cm. focus on to the prism of the Lummer plate; the distance between the condensing lens and the Lummer plate was 50 cm.

Measurement of Intensities.—The Lummer plate possesses some very particular advantages as an instrument for the determination of the intensity ratio of a hyperfine doublet of comparatively great separation. In the first place, the length of exposure necessary is short owing to the simplicity of the optical system, and its reasonably high relative aperture. Secondly, the intensity ratio of the doublet can be measured five or six times on each exposure, fringes corresponding to five or six successive orders of interference being measured. Finally, the illumination in the various parts of the fringe system of the Lummer plate is caused by the same original illumination (the image of the light source on the Twyman prism); while the various points in the fringe system of a Fabry-Perot étalon correspond to the illumination of different parts of the étalon, and consequently any inequality in the image of the light source gives rise to irregularities in the intensity distribution in the fringe system. The échelon grating also possesses this advantage, but has the disadvantage of requiring very much longer exposures (on account of the very low relative aperture). Where the highest resolving power is necessary and the intensity ratios of very close lines are to be measured the échelon grating is preferable; but where the lines are not very close (the cæsium hyperfine doublets are separated by an interval of $0 \cdot 30$ cm.$^{-1}$) the Lummer plate is more suitable.

A large number of photographs were taken of the lines 4555 and 4593, with an intensity scale applied to each plate, in the manner described below. In order to determine the effect of self-absorption on the intensity ratios, exposures were made over a wide range of vapour pressures of cæsium in the discharge tube. It will be seen that the influence of self-absorption at the lowest vapour pressure at which plates were made (about 5×10^{-4} mm. of mercury) is very small.

The method of determining intensities photographically was the same as that used by the author* in determining the intensities of the four components of the line 4101 of the indium arc spectrum. The relationship between the density of the image and the intensity of the illumination was determined in the following manner, for each plate used. A spectrograph of small dispersion was fitted with V-shaped slit. This was crossed by two wires, one of which was at the point where the width of the slit, was $0 \cdot 200$ mm. and the other where the slit was $1 \cdot 000$ mm. wide. With this spectrograph a continuous light source (a large pointolite lamp) was photographed. The result was a spectrogram of white light, the intensity of which increased continuously from top to bottom, and along which two lines ran, corresponding to the crosswires on the slit. The intensity of the light reaching the plate, at any given wavelength, is proportional to the width of the slit (since the illumination was continuous light), so that between the two parallel lines the illumination increases linearly from $0 \cdot 200$ to $1 \cdot 000$. The value of the intensity of illumination at any given point, for a given wave-length is determined by the equation

$$I = I_0 \{0 \cdot 2 + 0 \cdot 8 \, (x/y)\},$$

where I_0 is a constant (the intensity at the point where the slit width is $1 \cdot 000$ mm.); x is the distance (measured on the plate) of the point from the image of the crosswire at the slit width 0·200 mm., and y is the distance between the two images of the crosswires.

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* 'Z. Physik,' vol. 80, p. 59 (1933).

By setting the plate on the densitometer so that the required wave-length is in position and measuring the position of the densitometer slit for a number of different densities, the relationship between intensity of illumination and density of image is found. Over small intensity ranges the logarithmic density of the image when plotted against the intensity of illumination, gave nearly a straight line. The slope of the line changed with the time of development and the wave-length of light; but it was independent of the duration of the exposure. This was tested over a range of exposures of nearly 100 : 1. An exposure was made with a certain illumination; then on another part of the same plate an exposure was made with the intensity of illumination very much reduced and the duration of the exposure proportionally increased. The measurement of the plate after development showed that the curve connecting density and intensity was the same for both exposures. (This does not mean that a reduction in intensity and corresponding increase in time of exposure results in no change in density of image; this, of course, is not so; it only means that if in one exposure two different intensities give two specific densities of image, and in another exposure two intensities give two images of the same two specific densities, then the ratio of the intensities is the same in both exposures.)

Five of these intensity spectra were made on one end of a plate, the exposures varying between 1 and 3 minutes; on the other end of the plate the interference fringes were photographed, with exposures varying between 30 seconds and 12 minutes according to which line was photographed, and the vapour pressure of the cæsium. After developing the plate, two of the wedge spectra, possessing the range of densities present in the fringes, were selected at the required wave-length (4555 or 4593). These were measured on the densitometer, and the density-intensity curves found for the particular plate. These curves should of course give the same relationship and it was found that the intensity ratios given by one curve did not differ from those given by the other by more than 1%. The plates were developed in a tank, for a standard time at a temperature of 18° C. Throughout the course of the development the tank was very vigorously rocked, in order to avoid inequality of development. The edges of the plates were not used. The plates were 10 × 4 inches in size, a central part, 6 × 2 inches, was used for exposing, leaving a margin of 1 inch at the sides and 2 inches at the ends of the plate. This precaution was necessary owing to the fact that the edges of a plate are always rather less developed than the centre, and consequently have a density-intensity curve with a smaller slope.

In this way for every plate, curves were found giving the relationship between the density of image and the intensity of the illumination which gave rise to the image; and the intensity of a fringe could be found from its measured density. The densities of five or six of the fringes of each component in the photograph of the fringe system were measured on the photometer; the slit width of the beam of light passing through the fringe being about 0·03 mm., while the width of a fringe was between 0·07 mm. and 0·10 mm. Owing to the extreme sensitivity of the photoelectric cell (the cell was made specially by the Oxford Instrument Company) used in the photometer, there was no difficulty in working with so narrow a slit width. The length of the image of the slit on the plate was 0·7 mm.

In addition to the density, the position of each fringe was measured. This was necessary because in the successive fringes of the system the intensity becomes gradually greater as the order of interference (the angle which the emerging ray makes with the surface of the Lummer plate) increases. As a result of this it is not possible to make a direct comparison of the intensities of two components. However, this difficulty is easily overcome by a simple process of extrapolation.

Let the positions of the fringes of the shorter wave-length component, corresponding to the nth and $(n+1)$th order of interference be respectively x_n and $x_{(n+1)}$ and their intensities I_n and $I_{(n+1)}$; and the corresponding values for the longer wave-length component $x'_{(n)}$ and $x'_{(n+1)}$, and I'_n and $I'_{(n+1)}$. Then the true intensity ratio of the two components is given by the formula

$$I'_n \Big/ I_n + \left\{ (I_{(n+1)} - I_n) \frac{(x'_n - x_n)}{x_{(n+1)} - x_n} \right\},$$

or alternatively

$$I'_{(n+1)} - \left\{ (I'_{(n+1)} - I'_n) \frac{(x'_{(n+1)} - x_{(n+1)})}{x'_{(n+1)} - x'_n} \right\} \Big/ I_{(n+1)}.$$

In order to illustrate this process an example of a series of measurements and calculations is given in Table I. Column I contains the orders of interference of the various fringes measured; n, $n+1$, $n+2$, etc., being the shorter wave-length components and n', $(n+1)'$, $(n+2)'$, etc., being the longer wave-length components. Column II gives the positions of the fringes. Column III contains the measured densities in terms of length of an optical wedge. Column IV gives the intensities, derived from the density-intensity

Table I.

I.	II.	III.	IV.	V.	VI.	IVa.	Va.	VIa.
n'	4·00	2·55	—	0·55	—	—	0·48$_5$	—
$n+1$	4·64	2·32	0·51$_5$	(0·64)	1·24	0·45	(0·56)	1·24
$(n+1)'$	4·94	3·42	(0·55)	0·69	1·25	(0·48)	0·60	1·25
$n+2$	5·50	3·03	0·62$_5$	(0·76)	1·22	0·55	(0·67)	1·22
$(n+2)'$	5·78	4·05	(0·65)	0·80	1·23	(0·57)	0·70	1·23
$n+3$	6·31	3·52	0·70	(0·86)	1·22	0·62	(0·76)	1·22
$(n+3)'$	6·60	4·63	(0·73)	0·89	1·22	(0·64)	0·78	1·22
$n+4$	7·04	4·07	0·80	(0·94)	1·18	0·70	(0·82)	1·17
$(n+4)'$	7·26	5·03	(0·81)	0·96	1·18	(0·70$_5$)	0·83$_5$	1·19
$n+5$	7·74	4·18	0·82	—	—	0·71$_5$	—	—
			Mean value........		1·22	Mean value........		1·22
			Intensity ratio from plate = 1·22					

Example of measurements and calculations on an intensity plate.

curve, of all the fringes of the shorter wave-length component, the figures in brackets being the interpolated values given by the formula

$$I_n + \left\{(I_{(n+1)} - I_n)\frac{(x'_n - x_n)}{x_{(n+1)} - x_n}\right\}.$$

Column V contains the corresponding quantities for the longer wave-length component, and here again the figures in brackets represent the interpolated values given by the formula

$$I'_{(n+1)} - \left\{(I'_{(n+1)} - I'_n)\frac{(x'_{(n+1)} - x_{(n+1)})}{x'_{(n+1)} - x'_n}\right\}.$$

Column VI gives the ratio of the intensity of the long wave-length component to that of the short wave-length component. Columns IVa, Va, and VIa, give the same quantities as IV, V and VI but using a different exposure of the calibration wedge, to obtain the density-intensity curve.

By this method the intensity ratio is found in any individual plate as the mean of a large number of independent measurements. This is of very great value; for on account of purely irregular variations in the sensitivity of the emulsion in different parts of the photographic plate, individual intensity measurements are liable to erratic errors of about 3% or 4%, corresponding to errors of about 6% in intensity ratios. But by taking the mean of several independent determinations the effect of these purely erratic errors is very considerably reduced. In this work the intensity ratio given by each plate is found from about 10 independent intensity measurements. This probably reduces the erratic error to about 3%.

Table II contains the intensity measurements made on the line 4555 ($6S_{1/2} - 7^2P_{3/2}$). Column 1 gives the temperature of the cæsium at which the exposures were made. Column 2 shows the mean values for each individual plate; each of these figures represents the mean of about 10 separate ratios. Column 3 gives the mean of the values in Column 2. The greatest deviation from the mean of any individual determination is about 3%; the probable accuracy of the means is about 1%. Each mean represents the average of about 50 measurements. It can be seen that there is a small increase in the intensity ratio as the temperature decreases, the value at 100° being about 5% higher than that at 120°.

Table II.

Temperature °C.	Intensity ratios from individual plates.	Mean intensity ratios.
100	1·27 1·27 1·24 1·21 1·26 1·27 1·20	$1{\cdot}24_5$
110	1·20 1·20 1·25 1·24 1·24 1·22 1·22	$1{\cdot}22_5$
120	1·15 1·21 1·24 1·17 1·21 1·18 1·18	$1{\cdot}19_5$

Table III contains the measurements made on the line 4593 ($6S_{1/2} - 7^2P_{1/2}$). The accuracy of the individual determinations is not as great as those in Table II; for this line was very much weaker than the line 4555, and consequently fewer fringes were measured.

Table III.

Temperature °C.	Intensity ratios from individual plates.	Mean intensity ratios.
100	1·29 1·26 1·24	1·26
110	1·25 1·24 1·25 1·24 1·25	1·25
120	1·23 1·22 1·22	1·22
130	1·24 1·20 1·15 1·21	1·20

The average number of measurements for each plate was about six. The probable accuracy of the intensity ratio given by an individual plate is about

4%; the accuracy of the means is about 2%. It can be seen that the effect of increase in temperature on the intensity ratio is even smaller for this line than for the stronger lines.

Correction for Self-Absorption.—The slight increase of the intensity ratios as the temperature is reduced shows that there is a small amount of self-absorption; in order to estimate the quantitative effect of this it is necessary to know the values of the vapour pressure of cæsium at the various temperatures. A number of determinations have been made, of which the most important are those of Kroener,* Scott† and Langmuir and Kingdon.‡ They give widely differing figures, Kroener's being the lowest and Scott's the highest. In a recent work§ de Boer and Dippel discuss the merits of these determinations and conclude that the most reliable figures are those of Kroener. In Table IV the vapour pressures at the various temperatures at which intensity determinations were made, are given, calculated from the figures of Kroener, Langmuir and Kingdon, and Scott. In the last line of the table the ratios of the pressures at 130° to those at 100°, according to all three observers are given. It is very important that in spite of the great divergence in the absolute values, these ratios are all very nearly equal. It indicates that although the absolute values are not very reliable, the ratios of the vapour pressures at various temperatures are probably fairly accurate. And in the extrapolation to zero pressure, in order to find the intensity ratios when the effects of self-absorption are entirely absent, it is only necessary to know these ratios and not the absolute values. This

Table IV.

Temperature °C.	Vapour pressure in mm. Hg.		
	Kroener.	Langmuir and Kingdon.	Scott.
100	$4 \cdot 3 \times 10^{-4}$	$6 \cdot 7 \times 10^{-4}$	$1 \cdot 6 \times 10^{-3}$
110	$8 \cdot 1 \times 10^{-4}$	$1 \cdot 35 \times 10^{-3}$	$3 \cdot 0 \times 10^{-3}$
120	$1 \cdot 41 \times 10^{-3}$	$2 \cdot 40 \times 10^{-3}$	$5 \cdot 1 \times 10^{-3}$
130	$2 \cdot 69 \times 10^{-3}$	$4 \cdot 47 \times 10^{-3}$	$8 \cdot 7 \times 10^{-3}$
Ratio of vapour pressures at 130° and 100°	6·3	6·7	5·5

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* 'Ann. Physik,' vol. 40, p. 438 (1913).

† 'Phil. Mag.,' vol. 47, p. 32 (1924).

‡ 'Proc. Roy. Soc.,' A, vol. 107, p. 61 (1925).

§ 'Z. phys. Chem.,' B, vol. 21, p. 273 (1930).

will be seen clearly on the graphs showing the relationship between intensity and pressure. These graphs are shown in fig. 1.

In all three graphs the points of the intensities of both the doublets lie on straight lines. The slope of the line through the points (marked by crosses) representing the intensity ratios of the doublet comprising 4593 ($6S_{1/2} - 7^2P_{1/2}$) is smaller than that of the line through the points (marked by circles) representing the intensity ratios of the doublet comprising the line 4555 ($6S_{1/2} - 7^2P_{3/2}$). On all three graphs the lines give the value of the intensity ratios, for both doublets, at zero pressure, where the effects of self-absorption are entirely eliminated, as 1·27.

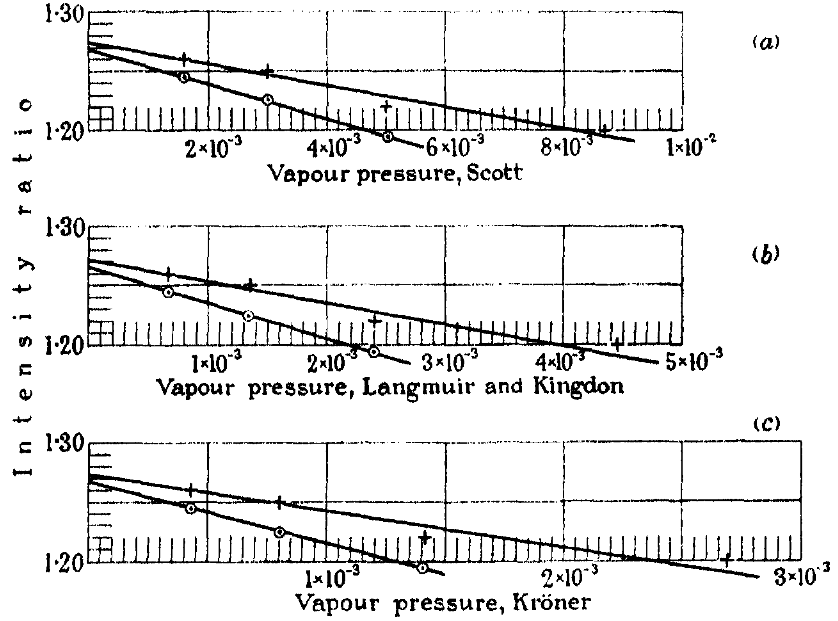

FIG. 1.

The correction applied in extrapolating to zero pressure from the lowest pressure at which measurements were made is only 0·02 for the stronger line, 4555. It is very improbable that this correction is wrong by more than about 50%; it cannot therefore introduce an error exceeding 0·01 into the value of the intensity of zero pressure. The correction for the weaker line, 4593, is even less, being only 0·01; consequently this cannot introduce an error greater than 0·005 into the value of the intensity ratio at zero pressure.

The probable accuracy of the values of the intensity ratio of the doublet comprising the stronger line, 4555, was shown above to be about 1%; while that of the doublet comprising the weaker line, 4593, was shown to be about

2%. The probable error of values for the intensities at zero pressure, where the influence of self-absorption is eliminated, is therefore 0·02, for both doublets. The intensity ratios of the two doublets are thus shown to be equal, and to have the value 1·27 ± 0·02.

The equality of the intensity ratios of the two hyperfine doublets is of the greatest importance, for the intensity ratio of the multiplet is anomalous. The expected value is 2 : 1, the observed value at the pressure corresponding to the lowest temperature (100° C.) at which measurements were made was found to be about 5 : 1. With increasing vapour pressure it becomes smaller. As the intensities of the hyperfine doublets agree, it is assumed that the anomalous behaviour of the intensity ratio of the multiplet does not affect the in the hyperfine structure.

The Value of the Mechanical Moment of the Nucleus.—It is well known that the intensity ratio of the two components of doublet of the type of either of the two doublets investigated is connected with the value of the quantized mechanical moment of the nucleus by the relationship

$$\text{Intensity ratio} = \frac{I+1}{I},$$

where I is the quantum number of the spin of the nucleus. The values for nuclear spins 5/2, 7/2 and 9/2 are :—

Spin		Intensity ratio
5/2	....	1·40
7/2	....	1·28
9/2	....	1·22
Observed value	....	1·27 ± 0·02

The observed value is in very good agreement with the value required by theory for the value I = 7/2. The theoretical value for I = 5/2 lies far above the limits of error, while the value for I = 9/2 lies far below the lower limit.

The value 7/2 for the mechanical moment is thus established with complete certainty. This is in agreement with Kopfermann's[*] measurements on the interval ratios in a few lines in the spark spectrum; he found 7/2 as the probable value, but on account of the difficulty of measuring the comparatively small intervals, was not able to exclude with certainty the value 9/2.

The author takes this opportunity to express his gratitude to Professor Lindemann for his continued encouragement in this and other researches carried out in his laboratory.

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[*] 'Z. Physik,' vol. 53, p. 437 (1932).

The Thermal Expansion of Bismuth by X-Ray Measurements.

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(Communicated by W. L. Bragg, F.R.S.—Received August 28, 1933.)

Introduction.

X-ray measurements recently carried out by the author on the lattice expansion of silver* and quartz† showed that the coefficients of thermal expansion, over the ranges investigated, are the same as those observed for the specimen as a whole using optical methods. Goetz and Hergenrother,‡ on the other hand, from X-ray measurements on the coefficients of thermal expansion of single crystals of bismuth, claimed to have found a large difference between values obtained by the two methods of measurement. A possible explanation of this is that their accuracy is not sufficient to establish definitely the difference claimed, as the experimental error is of the same order as that of the deviation of the X-ray measurements from the optical expansion curve. The author has since made X-ray measurements on the expansion of the bismuth lattice from room temperature to just below the melting point, and finds no evidence of such a discrepancy as Goetz and Hergenrother record.

Experimental.

X-ray powder photographs were taken in a camera* of the Debye-Scherrer type modified for work at high temperatures in which the specimen is heated by two surrounding furnaces, arranged one above the other with a small gap between them for the main X-ray beam to pass through and for the scattered rays to be recorded on a photographic film placed round the circumference of the camera. This arrangement of heating the specimen has been shown to give a uniform temperature throughout the scattering mass. In previous papers, I, the method of determining the temperature of a specimen for given conditions of heating by means of the lattice expansion of silver was described. Later experiments, II, on the thermal expansion of the quartz lattice showed that the method was a reliable one. During the present experiments the calibration of the camera was carefully checked with special reference to the range 20° C. to 300° C.

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* 'Proc. Phys. Soc.,' vol. 45, p. 635 (1933); *see also* 'Z. Kristallog.' (A), vol. 86, p. 106 (1933); quoted as I.

† 'Proc. Roy. Soc.,' A, vol. 142, p. 237 (1933); quoted as II.

‡ 'Phys. Rev.,' vol. 40, pp. 137, 643 (1932).

Filings were taken from a rod of pure bismuth,* sieved through a 250-mesh sieve and mounted on a thin fused silica rod which was supported vertically along the axis of the camera. The powder was thus held in the path of the X-ray beam and rotated throughout the exposure. The energy input in the furnaces was measured by the product of the current and the voltage drop across the furnaces. The temperature of the specimen was deduced from the measured energy input, being read off to 1° C. from the watts-temperature calibration curve drawn for the camera. In addition the temperature was taken at the inlet of the water supply for cooling the camera flanges and a correction made in cases where the temperature varied from the standard 18·5° C. Photographs were taken for a number of temperatures over the range from room temperature to 268° C. (melting point of bismuth 271° C.). An atmosphere of hydrogen was used in all experiments. To test the consistency of the observations the conditions were chosen at random, the order in which the photographs were taken not being the order of increasing temperature. This gives an opportunity of observing whether changes of lattice dimensions are reversible with temperature. The specimen was heated for 30 minutes at the desired temperature, to bring it to a steady temperature state and into thermal equilibrium with its surroundings, before the exposure was made.

Accuracy of Temperature Measurement.

The deviation of the experimental points on the watts-temperature calibration curve of the camera over the working range 20° C. to 270° C. is due to the combined effects of errors in the observed lattice spacing of silver and in the measurement of the input of energy in the furnaces. In the present investigation the deviation of points from which the calibration curve was constructed from a smooth curve corresponded to errors of 0·05 X units (1 in 80,000) in the lattice spacing of silver, which was taken as standard, or to 0·2 watts in the measured input of power to the furnaces. The estimated temperatures are probably correct with an error of not more than 1° C. to 2° C.

General Discussion.

The reflections on the powder photograph, taken with copper K_α radiation, were identified with the aid of data given by Davey,† Goetz, and Groth. It was unfortunate in the present work that the reflections whose positions were most dependent on the length of the principal axis were either weak or tended to overlap another line and for this reason it was not possible in all experiments to obtain an accurate estimate of the axial ratio. This was noticeable at the higher temperatures where the reflection 0 0 $15_{\alpha_1\alpha_2}$ (5 5 5-rhombohedral indices) became too weak for any high accuracy and the 2 1 13_{α_1} or 1 0 14_{α} overlapped the 5 0 2_{α_1}. On the other hand, since the axial ratio is large (2·61) the position of a line is comparatively insensitive to small changes in its value, and it is therefore still possible in the present experiments in spite of the difficulty of measuring the axial ratio with great precision to determine the value of d_{100}, the spacing of the 100 planes, very accurately, the estimated error being of the order of 1 in 50,000 or less than 0·1 X units. Values of c, the principal axial length, are only given for those temperatures at which a reasonably accurate determination could be made, the error being 1 in 30,000 to 1 in 20,000. The method* of plotting the measured spacing against the corresponding value of $\cos^2\theta$ for individual reflections and extrapolating by means of a straight line through the points to $\cos^2\theta = 0$ was used in the evaluation of the lattice spacing. The spacing values, given in Table I, are corrected for the effect of refraction of the X-rays in the specimen.

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* Metal supplied by A. Hilger, Ltd. Analysis: silver, 0·004%; other elements, minute trace; bismuth, by difference, 99·995%.

† 'Phys. Rev.,' vol. 25, p. 753 (1925).

Comparison of X-ray and Optical Measurements.

(*a*) *Expansion parallel to the principal axis.*—By the use of optical methods the thermal expansion of bismuth parallel to the principal axis has been measured by Fizeau,† Roberts,‡ and Ho.§ Roberts and Ho carried out experiments up to near the melting point and their results are in substantial agreement. The present X-ray results are, for reasons already stated, not given for temperatures above 150° C. Over this range of temperatures the mean coefficient of expansion is $16\cdot9 \pm 0\cdot5 \times 10^{-6}$. Fizeau gives $16\cdot4 \times 10^{-6}$ (0–80° C.), Roberts $16\cdot3 \times 10^{-6}$ (0–150° C.), and Ho $16\cdot6 \times 10^{-6}$ (20–150° C.). The agreement of the present X-ray result with the above values is good in view of the difficulties encountered.

(*b*) *Expansion perpendicular to the principal axis.*—It is in this direction in which the spacing can be measured accurately that we find some interesting results. The curve giving the lattice spacing d_{100} in terms of the temperature

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* Bradley and Jay, 'Proc. Phys. Soc.,' vol. 44, p. 563 (1932).

† 'C. R. Acad. Sci. Paris,' vol. 68, p. 1125 (1869).

‡ 'Proc. Roy. Soc.,' A, vol. 106, p. 385 (1924).

§ See reference to Goetz and Hergenrother.

Results.

Table I.—Expansion of Bismuth in directions parallel and perpendicular to the Principal Axis.

Order of experiment.	Temperature of specimen. ° C.	Lattice spacing* (X units).	
		c.	d_{100}.
3	18·5	11836·3†	3928·7
15	26	11837·1	3928·9
9	46	—	3929·7$_5$
11	68	—	3930·7
2	78	11848·0	3931·4
16	89	11850·1	3932·0
14	114	11854·5	3933·2$_5$
4	140	11860·9	3934·2$_5$
17	164	—	3935·5
19	191	—	3936·7
8	203	—	3937·4
7	207	—	3937·4$_5$
1	230	—	3938·6
12	239	—	3939·1
5	246	—	3939·4
18	248	—	3939·2
6	253	—	3939·2$_5$
10	259	—	3939·3$_5$
13	265	—	3939·5
20	268	—	3939·7

* Corrected for refractivity.

† Compare the value 3·9453 A (111 rhombohedral indices), which is equivalent to 11·8359 A. (001 hexagonal indices), given by Goetz and Hergenrother at 21° C.

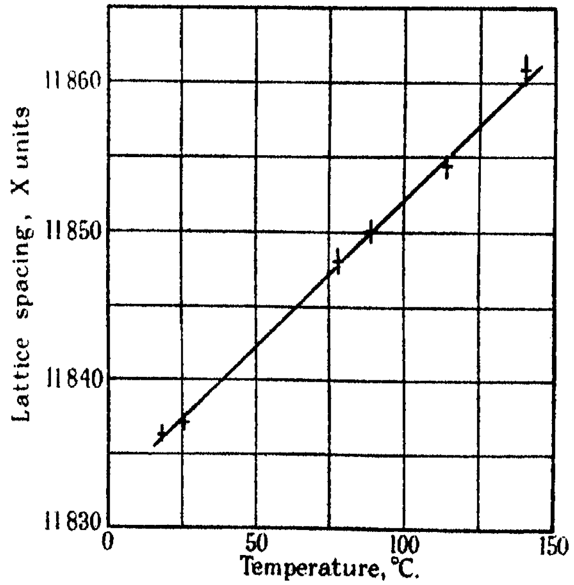

Fig. 1.—Expansion parallel to the principal axis.

is shown in fig. 2. Over the range 20° C. to 240° C. the mean coefficient of thermal expansion is $12 \cdot 0 \pm 0 \cdot 2$ which agrees with the value given by Roberts for the same range of temperature. Above 250° C. the curve falls considerably below that corresponding to a continued linear expansion.* This phenomenon was also found by Roberts from his optical measurements. The curve also shows a sudden expansion between 70° C. and 80° C., which suggests a connection with the supposed allotropic change point around 75° C.† Although the effect is only small, yet the consistency of the observations above and below 75° C. lends support to the view that it is genuine.

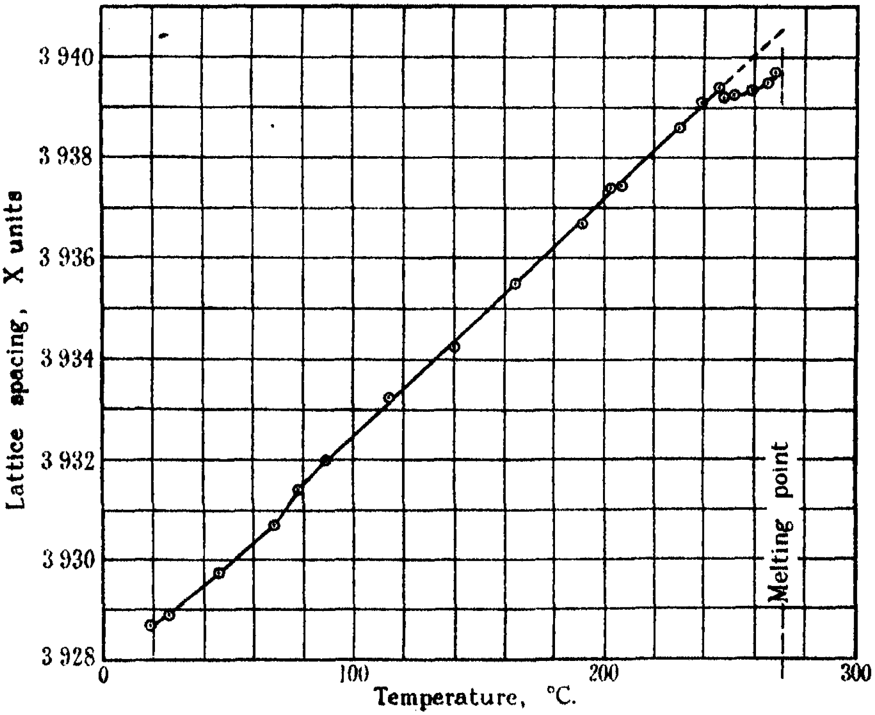

FIG. 2.—Expansion perpendicular to the principal axis.

The characteristics of the results of the present X-ray measurements in a direction perpendicular to the principal axis may be summarized as follows:

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* Goetz, from measurements on the expansion along the principal axis, claimed to have found a progressive increase in the coefficient of expansion of the lattice right up to the melting point.

† Cohen and Moesveld, 'Z. phys. Chem.,' vol. 85, p. 419 (1913); Wurschmidt, 'Ber. deut. phys. Ges.,' vol. 15, p. 1027 (1913); Goetz and Hasler, 'Phys. Rev.,' vol. 36, p. 1752 (1930).

A steady expansion up to 70° C., a sudden rise between 70° C. and 80° C., a uniform expansion from 80° C. up to 240° C. and a decided falling off in the coefficient of expansion above 250° C.

The results, given in Table II, are obtained from a curve in which the lattice spacings expressed in terms of unit length ($3928 \cdot 7_0$ X units) are plotted against the corresponding temperatures.

Table II.

Expansion in terms of unit length at 20° C. $\times 10^{-4}$.	Temperature. ° C.	Range of temperature. ° C.	Mean coefficient of expansion. $\times 10^{-6}$.		
0·0	20	50	11·0 ± 0·5*		12·0 ± 0·2
5·5	70				
7·2	80	80	11·9 ± 0·3	12·1 ± 0·2	
16·7	160	80	12·3 ± 0·3		
26·5	240				

* Compare $12 \cdot 1 \times 10^{-6}$ at 40° C. given by Fizeau, 'C. R. Acad. Sci. Paris,' vol. 68, p. 1125 (1869), and $10 \cdot 36 \times 10^{-6}$ at room temperature given by Bridgman, 'Proc. Nat. Acad. Sci. Wash.,' vol. 10, p. 411 (1924).

Allotropy of Bismuth at 75° C.

The recent work by Ho on the macroscopic expansion of bismuth shows a small discontinuity in the coefficient of expansion at 75° C., which he associates with the allotropic change. The present X-ray measurements* also show a small jump in this neighbourhood and support the view that an allotropic change is connected with a lattice modification. It can be seen from the order in which the observations were made that the phenomenon is reversible.

Changes just below the Melting Point.

The results of observations made at temperatures above 250° C. while agreeing with those obtained from optical measurements do not allow of a simple explanation. A suggestion made by Roberts to explain his results is that a certain number of bismuth atoms, which possess energies equivalent to those of molten bismuth atoms and characterized by a smaller volume than atoms of solid bismuth, reacting on the crystal lattice cause a falling off in the expansion.

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* Goetz found no such effect from his X-ray measurements. This was not surprising in view of the possibility of deviations of 0·01% in lattice spacing from a smooth curve.

Following up this idea one might expect at some temperature the lattice spacing to decrease until just before complete melting a state is reached where the lattice dimensions are comparable with the packing of liquid bismuth atoms. The continued expansion, though at a smaller rate, does not appear to bear out this supposition. Another possibility is that an allotropic change occurs at about 245° C. to 250° C., which is shown by the drop in lattice spacing and the much smaller expansion up to near the melting point. It is, however, difficult to associate this phenomenon with the cubic modification suggested by Kapitza* as existing just below the melting point, and since shown to be unnecessary by the work of Webster.† No indication of a parameter change which would account for this cubic modification was given by the intensities of reflections. The presence of impurities, originally in the bismuth and later acquired during the experiments, affecting the high temperature measurements is another possibility.

Whatever the true explanation of the phenomenon the observed changes are reversible and appear to be consistent.

Acknowledgments.

I wish to thank Professor W. L. Bragg, F.R.S., and Dr. A. J. Bradley for their encouraging interest in the work which was carried out in the Physical Laboratories of the University of Manchester. My thanks are also due to Mr. A. P. M. Fleming, C.B.E., Director-Manager, Research and Education Departments of the Metropolitan-Vickers Electric Company, Ltd., for his kind and helpful interest.

Summary.

X-ray powder photographs of bismuth have been taken at temperatures ranging from 18·5° C. to 268° C. (melting point of bismuth 271° C.), and the lattice dimensions calculated for each temperature observation. The lattice expansions are compared with those found by the use of optical methods.

Roberts from optical measurements found an almost linear expansion up to 240° C., followed by a decrease in the coefficient of expansion near the melting point. These characteristics were later confirmed by Ho, who in addition found evidence of a discontinuity in the coefficient of expansion at 75° C. which he associated with an allotropic change. Goetz and Hergenrother, from X-ray measurements with single crystals, found no evidence either of a

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* 'Proc. Roy. Soc.,' A, vol. 119, p. 358 (1928).

† 'Proc. Roy. Soc.,' A, vol. 133, p. 162 (1931).

lattice discontinuity at 75° C., or of a decrease in the coefficient of expansion near the melting point. Their results showed a progressive increase in the coefficient of expansion of the lattice from room temperature right up to the melting point. The results of the present X-ray measurements made with bismuth powder disagree with the findings of Goetz and Hergenrother and show that the lattice expansion agrees with the expansion of the specimen as a whole. Briefly the characteristics of the expansion curve are a steady expansion from 20° C. to 70° C., a sudden rise between 70° C. and 80° C., a linear expansion up to 240° C., and above 250° C. a decrease in the coefficient of expansion.

The nature of the changes in the lattice dimensions just below the melting point are discussed.

Continuous Absorption of Light in Cæsium Vapour.

By H. J. J. Braddick, Ph.D., and R. W. Ditchburn, Ph.D., Professor of Experimental Philosophy, Trinity College, Dublin.

(Communicated by J. Chadwick, F.R.S.—Received September 22, 1933.)

(1) *Introduction.*

A region of continuous absorption lying on the short wave-length side of the limit of the principal series and corresponding to the photo-ionization of the atom is to be expected in the alkali metal vapours. The currents due to photo-ionization have been measured* and several attempts have been made to observe the absorption.† The main difficulty is in the action of the vapour on the windows of the absorption cell. This has usually been overcome by keeping the ends of the absorption tube cool and checking the diffusion of the vapour from the centre of the tube by means of a foreign gas. This gas produces a large and complicated effect on the absorption (Harrison†). In the present experiments it has been found possible to avoid the use of a foreign gas by employing a long absorption tube and a low vapour pressure. Cæsium was used because it gives a sufficient pressure at a moderate temperature and because its series limit lies in the most convenient region of the spectrum.

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* For references see p. 479.

† Harrison, 'Phys. Rev.,' vol. 24, p. 466 (1924); Ditchburn, 'Proc. Roy. Soc.,' A, vol. 117, p. 486 (1928); Trumpy, 'Z. Physik.,' vol. 47, p. 804 (1928); vol. 71, p. 720 (1931); Mohler and Boeckner, 'Bur. Stand. J. Res.,' vol. 3, p. 303 (1929).

(2) *Experimental.*

(*a*) *General Arrangement.*—The general arrangement of apparatus is shown in fig. 1. Light from the source S is collimated by means of the lens L_1. It passes down the absorption tube and is focussed by the cylindrical lens L_2 on the slit (P) of the spectrograph. Throughout an experiment the absorption tube was maintained at about 280° C. The pressure of the vapour was controlled by the temperature of the side tube which varied from about 220° C. to 255° C. in different experiments. On each plate spectra were taken—

(*a*) with the side tube hot;
(*b*) with the side tube cold;
(*c*) with the side tube cold and a grid G inserted to reduce the light in a known ratio.

This provides data for calibrating the plate and measuring the absorption.

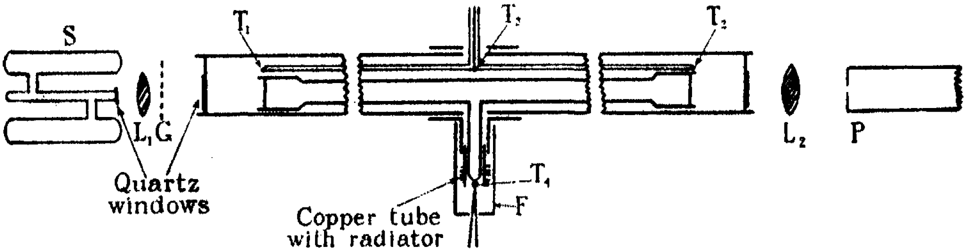

Fig. 1.—Furnace windings and laggings omitted.

(*b*) *Temperature Control.*—The absorption cell was a fused quartz tube 2 metres long and 1 cm. in diameter. The ends were enlarged and closed with polished discs of fused quartz sealed in as shown in fig. 1. The design enables us to use the full aperture of the long tube because the part of the window traversed by the light is not distorted by sealing-in. The quartz tube rested on V supports inside a copper tube. The copper tube rested by flanges inside a steel tube which carried the heating winding. The whole was heavily lagged with asbestos string. This furnace was made in two parts united at the centre by a steel T-piece carrying an independent winding. The side arm of this T-piece projected into the side furnace F. The temperature distribution was explored with a thermocouple and we were able to satisfy ourselves that, with proper adjustment of the heating currents, the coldest part of the closed system was at the extreme end of the side tube. The temperature of the main tube was measured during the experiment by chromel-alumel couples T_1, T_2, and T_3. Since the vapour pressure varies rapidly with temperature it was necessary to measure the temperature of the side-tube with some accuracy. The thermocouple T_4 was a Pt/Pt-Rh thermocouple whose cold junction was immersed in boiling naphthalene. The difference of temperature between the naphthalene point (218° C.) and T_4 (218-250° C.) was fairly small. It was measured by a compensation circuit and a sensitive galvanometer.* The arrangement was calibrated at the tin freezing point (232° C.). It gave an accuracy of 0·1° C. corresponding to 0·4% on the vapour pressure.

(*c*) *Preparation of Cæsium.*—The cæsium metal for the earlier experiments was prepared by distilling CsCl with metallic calcium. In order to remove the suspicion that part of the absorption might be due to an impurity a set of experiments was done with a different absorption tube and the metal prepared by the azide method.† In each experiment the quartz tube was outgassed and the cæsium was refluxed before being distilled into the tube.

(*d*) *Light Sources.*—Three different light sources were used. A hydrogen capillary discharge tube of the shape shown was used to provide a continuous background. It was useful from λ 3300 to λ 2200. The discharge was produced by a 3000-volt transformer and the primary current was kept constant by hand regulation. After the discharge had been run for about 15 minutes the intensity was constant as far as we could detect by photographic photometry. For measurements at shorter wave-lengths the source was a condensed aluminium spark. The spark passed between the edges of coplanar aluminium discs rotated at about 100 r.p.m. It was maintained by a large induction coil used as a transformer. Tests showed that this source could be kept constant to within about 2%. A water-cooled Cooper-Hewitt mercury arc was used as a source for more accurate observations at a number of isolated wave-lengths. The arc stream was deflected against the wall of the tube by an electromagnet in series with the arc. The choking effect of the magnet was favourable to steadiness and it prevented the irregular condensation of mercury.

(*e*) *Photographic.*—The spectrograph was a small Hilger quartz instrument (E.31). Ilford Process plates (unbacked) were used for wave-lengths above 2400 A. Below this wave-length their contrast decreases rapidly. So for experiments on this region the plates were sensitized by bathing with molten *yellow* vaseline. After bathing the plates were allowed to drain for several hours in an incubator at about 45° C. Before development the plates were washed very thoroughly in warm benzene. If at any stage of the process the plates were heated above 50° C., they were found to be fogged and in order to lower the melting point of the vaseline it was mixed with about 10% of medicinal paraffin. Plates treated in this way were found to be more reliable for quantitative photometry than plates sensitized with oils in solution or commercial ultra-violet sensitive plates.

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* The naphthalene boiler was constructed in accordance with the specifications for secondary standards given in the 'Dictionary of Physics' (vol. 1, p. 704).

† Suhrman and Clusius, 'Z. anorg. Chem.,' vol. 152.

The plates were developed with borax M-Q developer (Wellington formula) in a tank designed to give rapid flow of the developer over the plate.*

(*f*) *Photometry.*—Seventeen spectra were taken on each plate. The four lying nearest the edges were rejected. To reduce errors due to plate variation the absorption spectra were placed among the comparison spectra. To detect and eliminate errors due to changes in the optical system (*e.g.*, transparency of windows) some of the comparison spectra were taken before and some after the absorption spectra. The plates were measured on a Moll microphotometer (type A). The photometer readings for the continuous spectra were automatically recorded. The absorptions were calculated by linear interpolation as described below using a single grid with about 20% absorption.

Photometer readings for line spectra were taken by eye, the clear plate being read on both sides of the line. Three grids were used and the vapour pressures were adjusted so that the absorption at the wave-length under investigation was approximately equal to that produced by one of the grids. The small differences were then obtained by interpolation. Plates which did not show a good internal consistency were rejected.

The absorption coefficient is proportional to $(2 - \log_{10} \mathrm{T})$ where T is the percentage of light transmitted by the vapour.† The absorption as defined by this formula was calculated for the grids.‡ An approximately linear relation was found between the photometer readings and the absorption. The absorption of the vapour could thus be determined by interpolation.

(3) *Results.*

(*a*) *Variation of Absorption with Vapour Concentration.*—All the absorptions measured for a particular wave-length were plotted against the vapour concentration (*i.e.*, the vapour pressure corrected for the difference between the temperature of the absorption tube and a standard temperature). It was found that within the limits of error the absorption was proportional to the concentration at all wave-lengths. The graphs for λ 1990 and λ 3184 are shown in fig. 2.

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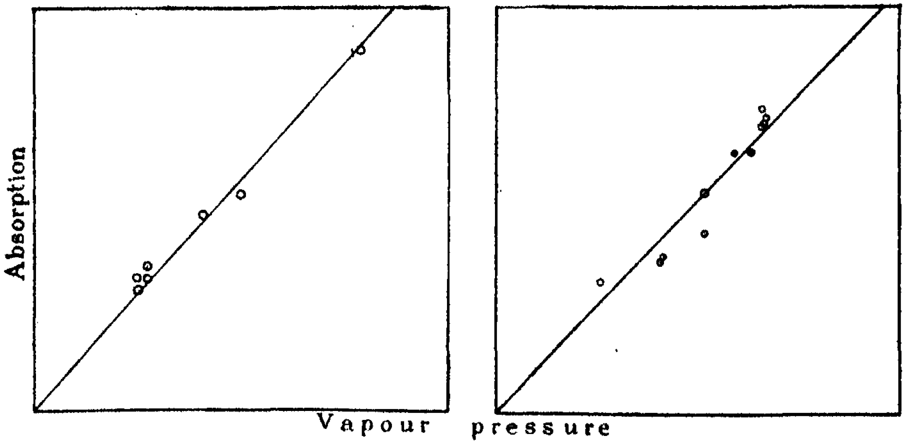
* Dobson, Griffiths, and Harrison, "Photographic Photometry," p. 77.

† Ditchburn, 'Proc. Roy. Soc.,' A, vol. 117, p. 486 (1928).

‡ An account of these will be published shortly by Braddick.

(*b*) *Variation with Wave-length.*—The atomic absorption coefficients calculated from the above graphs are shown plotted against wave-length in fig. 3.

(*c*) *Absolute Value of the Absorption and Accuracy of Results.*—The most accurate absolute value was obtained at λ 3130. The value at this wave-length is more accurate than the value at the limit because the form of the curve at the limit makes observations with the continuous light source difficult and there is no suitable line nearer than λ 3130. The value for the atomic coefficient obtained is $1 \cdot 94 \times 10^{-19}$ cm.$^{-1}$ at λ 3130. This depends on a formula for the vapour pressure given by Rowe.* Excluding uncertainties in the vapour pressure formula the uncertainty in the value should not exceed ±4%. We think the result is probably correct within half this error. The best value for the absorption at the limit is $2 \cdot 18 \times 10^{-19}$ cm.$^{-1}$. The possibility that the absorption rises sharply to a much larger value just at the limit cannot be completely excluded since the shape of the observed curve may be conditioned by the finite resolving power of the spectrograph. We believe that this sharp rise does not exist, since the shape of the curve was not affected by altering the width of the spectrograph slit. The curve drawn is almost certainly correct to within a few Angstroms of the limit on the short wave-length side.



λ 1990 λ 3184

Fig. 2.

The accuracy of other parts of the curve is more difficult to estimate. In the region of the minimum the small absorption makes work more difficult.

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* 'Phil. Mag.,' vol. 3, p. 534 (1927).

It is difficult to fix the wave-length of the rather flat minimum. We think it certainly lies between λ 2820 and λ 2700, the most probable position being λ 2800. The lowest absorption is very probably between 35% and 45% of the absorption at λ 3130. The measurements at low wave-lengths are technically more difficult, but we think the curve at λ 1990 and λ 1935 is correct to ±5%. Very few readings were taken between λ 2300 and λ 2000 and this part of the curve is, in fact, an interpolation confirmed by a few rough readings.

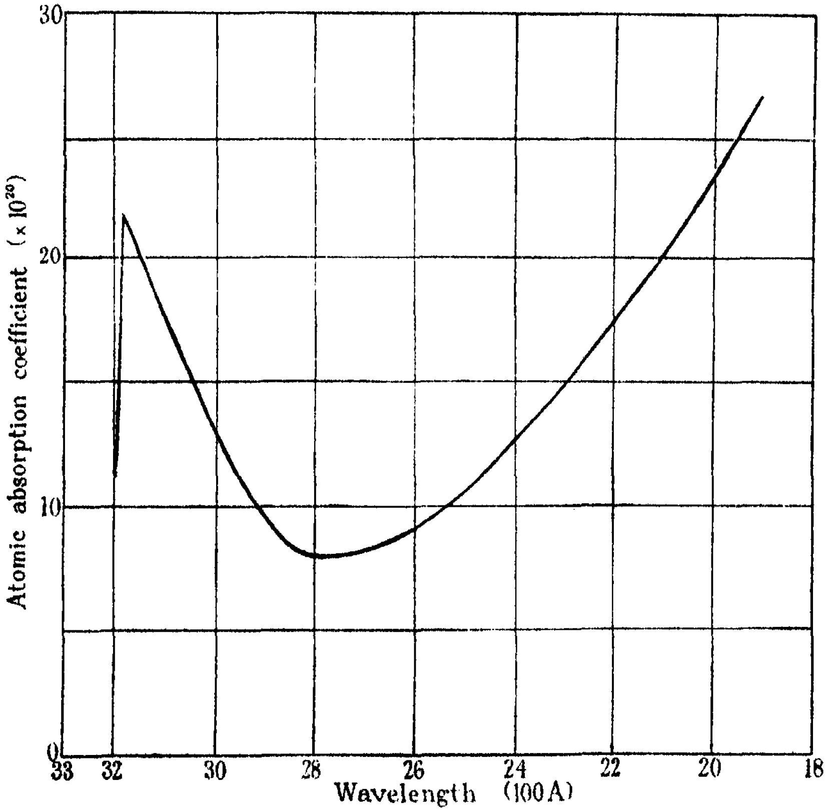

FIG. 3.

(*d*) *Absorption on the Long Wave-length Side of the Limit.*—This region really requires a special study with an instrument of higher resolution. We were able to observe the absorption of the series lines up to the 17th member of the series.

The shape of the curve in the neighbourhood of the limit is shown roughly in fig. 4. It will be seen that as the series lines run together the absorption tends to a value about 1×10^{-19} cm.$^{-1}$ and that there is an abrupt rise to more than twice this value at the limit. This does not agree with the theoretical calculations of Sugiura* who predicts no discontinuity in absorption at the limit.† In view of the low resolving power of our apparatus our conclusion on this point must be regarded as tentative, but a similar conclusion is suggested by the curve published for lithium by Trumpy.‡

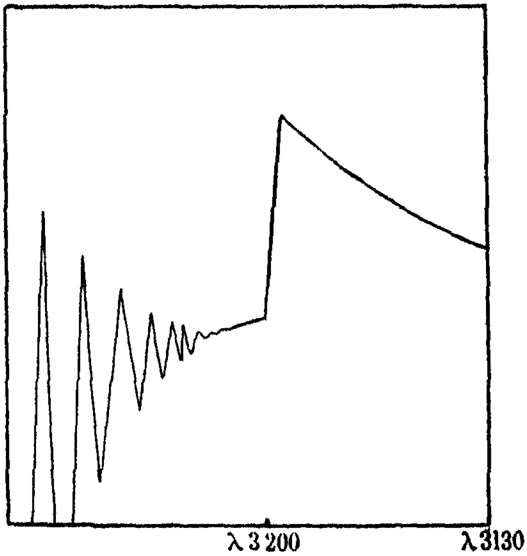

FIG. 4.

(4) *Discussion.*

The absorption at every wave-length is a linear function of the concentration of atoms. This suggests strongly that all the absorption is due to atoms. This is surprising since all theoretical calculations on atomic absorption predict a monotonic decrease from the series limit in the direction of short wave-length. We have considered two alternative explanations. Firstly, part of the absorption may be due to an impurity, present in excess and forming reversibly a molecule CsX. (The number of such molecules would be proportional to the number of cæsium atoms.) This possibility is practically excluded by the repetition of the results using different methods of preparing the cæsium.

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* 'J. Phys. Rad.,' vol. 8, p. 113 (1927).

† His curve shows a discontinuity in slope but not in magnitude.

‡ 'Z. Physik,' vol. 71, p. 720 (1932).

Secondly, part of the absorption may be due to an adsorbed film of cæsium atoms on the windows of the absorption cell, the film being in equilibrium with vapour. This was tested experimentally by measuring the absorption produced in a cell 4 cm. long. The absorption was zero within experimental error and we conclude that the results of the main experiment are not affected by an adsorbed film.*

The results may be compared with those obtained on the photo-ionization of cæsium vapour.† This has been investigated by two methods: the direct measurement of the photo-electric current and the space charge magnification method.‡ The former only is suitable for absolute measurements. Our value at λ 3130 ($1 \cdot 94 \pm 0 \cdot 1 \times 10^{-19}$ cm.$^{-1}$) agrees well with the absolute value obtained by Mohler and Boeckner§ ($1 \cdot 85 \times 10^{-19}$ cm.$^{-1}$) probably with a similar range of error. It therefore appears that the absorption in this region is all due to the photo-electric process.

The shape of our curve agrees well with that obtained by Little (*loc. cit.*) and by Cooke (*loc. cit.*) by the direct method. Mohler and Boeckner using the magnification method found a smaller rise in the region below λ 2600 and Lawrence and Edelfsen using a higher magnification found no rise in this region. It seems probable that this discrepancy is produced by a decrease in magnification of the space-charge method at short wave-length.

It thus appears that the absorption at all wave-lengths is due to photo-ionization. Accepting this conclusion and combining the absorption and photo-current data the linear dependence on vapour pressure is established over a very wide range. The range from 0·6 mm. vapour pressure to 0·006 mm. is covered by our experiments and those of Mohler and Boeckner. In this connection it should be noted that we have used the same vapour pressure formula as Mohler and Boeckner. While there are large discrepancies between the values of the vapour pressure found by different observers, there is fair agreement about the variation with temperature.|| The conclusion that the absorption at low wave-lengths is atomic is further supported by the experiments of Little (vapour pressure 0·03 mm.), Cooke (vapour pressure 10^{-4} mm.)

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* Golub and Kondratjew, 'Phys. Z. Sowjet. Union.,' vol. 1, p. 619 (1932), found absorption due to adsorbed films in NO_2, but failed to find it with sodium.

† Mohler, Foote, and Chenault, 'Phys. Rev.,' vol. 27, p. 37 (1926); Little, *ibid.*, vol. 30, p. 109 (1927); Lawrence and Edelfsen, *ibid.*, vol. 34, p. 233 (1929); Mohler and Boeckner, 'Bur. Stand. J. Res.,' vol. 3, p. 303 (1929); Cooke, 'Phys. Rev.,' vol. 38, p. 1351 (1931).

‡ Foote and Mohler, 'Phys. Rev.,' vol. 26, p. 195 (1925).

§ *Loc. cit.* Their value is confirmed as regards order of magnitude by Cooke.

|| Mohler and Boeckner, *loc. cit.*, p. 312.

and Kunz* (vapour pressure 10^{-6} mm.) who all find an increase in the photo-ionization probability at wave-lengths below λ 2700.

Theoretical calculations of the photo-ionization probability in hydrogen and the alkali-metals based on the wave mechanics have been made by Sugiura,† Trumpy,‡ Hargreaves,§ Gaunt,‖ and Phillips.¶ None of these calculations refers directly to cæsium, but it is usually assumed that the form of the absorption curves should be generally similar for all atoms with a single valence electron. All calculations agree in showing a monotonic fall in the absorption coefficient from a point near the limit towards low wave-lengths. Miss Phillips' work was specially directed to see if there could be an increase in the atomic absorption at short wave-lengths for potassium. She concluded that no reasonable form of the atomic field would explain an increase. The curves obtained experimentally by Lawrence** and by Ditchburn for†† potassium show a rise even larger than that obtained for cæsium.

We have considered the possibility that the discrepancy between theory and experiment might be due to some second photo-ionization process‡‡ (*e.g.*, photo-ionization accompanied by an internal transition) starting about λ 2800. But this process would not be probable with the energy available. It should further be noted that even in the neighbourhood of the limit the form of our curve does not agree with theoretical calculation. Empirically we find that from the limit to λ 2800 the absorption is proportional to λ^8 within experimental error. This is a much more rapid variation than that given by theory.

It is interesting to consider the reverse process, *i.e.*, the capture of an electron by a Cs^+ ion. By the principle of detailed balance we obtain the relation§§

$$q(v) = \frac{\nu^2}{v^2} k(\nu) \times \text{const.},$$

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* 'Bull. Amer. Phys. Soc.,' vol. 8, p. 18 (1933).

† 'J. Phys. Rad.,' vol. 8, p. 113 (1927); 'Phil. Mag.,' vol. 22, p. 495 (1927).

‡ 'Z. Physik,' vol. 54, p. 372 (1929); vol. 71, p. 720 (1931).

§ 'Proc. Camb. Phil. Soc.,' vol. 25, p. 75 (1929).

‖ 'Proc. Roy. Soc.,' A, vol. 126, p. 654 (1930).

¶ 'Phys. Rev.,' vol. 39, p. 905 (1932).

** 'Phys. Rev.,' vol. 34, p. 1056 (1929).

†† 'Proc. Roy. Soc.,' A, vol. 117, p. 486, (1928).

‡‡ It should be noted that owing to the difference in composition of the light used in the experiments processes involving the simultaneous absorption of two quanta are excluded.

§§ Milne, 'Phil. Mag.,' vol. 47, p. 209 (1925); see also Mohler and Boeckner, *loc. cit.*, p. 313.

where $k(\nu)$ is the absorption coefficient for frequency (ν) and $q(v)$ is the capture cross-section for electrons of velocity v.

Using this equation we have calculated from our absorption curve the dependence of $q(v)$ on v. This curve shows a minimum at 0·86 volts. We suggest that the capture of the electron by the ion may be regarded as a collision in which the electron loses the appropriate amount of energy. We should then expect the capture probability to be in some respects similar to the collision probability between an electron and the neighbouring rare gas. No data are available for xenon, but helium, neon, and argon all show a minimum a little under 1 volt.* It may thus be expected that wave-theory consideration which give this Ramsauer effect may also explain our results.

We are indebted to the Purser Fund of Trinity College for a grant to purchase the microphotometer.

Summary.

(1) The absorption of light in cæsium vapour is measured from the series limit (λ 3184) to λ 1935.

(2) The absorption at all wave-lengths is directly proportional to the pressure. The absorption decreases from the limit to λ 2750 and then rises monotonically to the lowest wave-length observed.

(3) The value of the atomic absorption coefficient at the limit is $2 \cdot 2 \pm 0 \cdot 1$ cm.$^{-1}$. This agrees with the value deduced by Mohler and Boeckner from measurements of the photo-ionization. Thus the whole of the absorption appears to be photo-electric.

(4) Special experiments showed that the absorption in the farther ultra-violet was proportional to the vapour pressure of cæsium. The rise thus appears to be of atomic origin.

(5) No appreciable part of the absorption is due to adsorbed films of cæsium on the windows.

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* Normand, 'Phys. Rev.,' vol. 35, p. 1217 (1930).

Gaseous Combustion in Electric Discharges. Part IX.*—*The Cathodic Water-Gas Equilibrium.*

By G. I. Finch, B. W. Bradford, and R. J. Greenshields, Imperial College of Science.

(Communicated by W. A. Bone, F.R.S.—Received September 28, 1933.)

Introduction.

It was pointed out in Part VII* of this series that, in addition to the experiments of which accounts have been set forth therein and in Part VIII,* it would be necessary to carry out an investigation of the cathodic equilibrium between steam and carbonic oxide in order to elucidate the mechanism of the role played by hydrogen in promoting the cathodic combustion of carbonic oxide-oxygen mixtures.

Experimental.

A high-tension, direct current arc was maintained between gold or tungsten electrodes, *i.e.*, sputtering and non-sputtering metals respectively, in stagnant CO-O_2-H_2 mixtures until equilibrium had been attained. The gaseous products were analysed and the compositions of the equilibrium mixtures determined. The gap width and current conditions were such that chemical action was practically wholly confined to the cathode zone of the discharge (see Parts I and III).

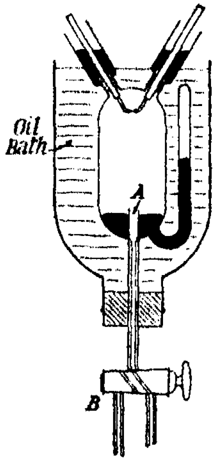

Fig. 1.

Apparatus.—The reaction vessel employed is shown in fig. 1. In order to prevent condensation of steam, the vessel was immersed in an oil bath maintained at 61° C. in all experiments. The saturation temperature corresponding to the highest partial pressure of water vapour formed in any experiment was 31° C. Dead-gas space was eliminated in the manner indicated in fig. 1, by filling the inner tube, A, with mercury during the progress of a combustion. The two-way tap, B, gave access to the pumping system and gas-holders and to a gas-sampling tube. The gases were dried before admission to the reaction vessel by passage over redistilled phosphoric oxide, the requisite mixtures being made up in the reaction vessel. Impurities were less than 0·2% and consisted in the main of adventitious nitrogen. In calculating rates of reaction, changes in the effective reaction vessel volume due to displacement of mercury into the manometer were duly allowed for.

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* 'Proc. Roy. Soc.,' A, vol. 133, p. 173 (1931) (Part VIII); wherein references are given to the preceding parts.

Procedure.—The reaction vessel was filled to the desired pressure with a suitable mixture of electrolytic gas and carbonic oxide, or hydrogen and carbon dioxide, whereupon the rate of change in pressure was observed during cathodic combustion until the pressure had become constant. The residual gas mixture was then sampled and analysed in a Bone-Newitt apparatus. The initial compositions of the gas mixtures employed were equivalent to $2H_2 + O_2 + 1$, 2 or 3 CO, or mixtures of carbon dioxide and hydrogen in corresponding proportions. Irregular rates of combustion were observed for the interaction of hydrogen with carbon dioxide, probably owing to the prevalence of erratic positive column combustion in the earlier stages of each such experiment. In most experiments equilibrium was attained from the carbonic oxide side of the reaction, approach by the combustion of carbon dioxide, and hydrogen being, for reasons previously outlined, only resorted to occasionally in order to obtain a check.

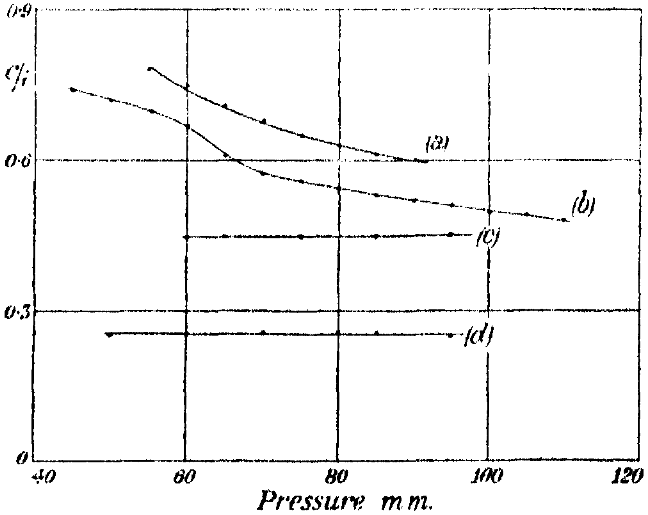

Fig. 2.—(a) $3CO + O_2 + 2H_2 : \overline{W}$; (b) $2CO + O_2 + 2H_2 : \overline{W}$; (c) $CO + O_2 + 2H_2 : \overline{W}$; (d) $2CO + O_2 + 2H_2 : \overline{Au}$.

The Results.

It will be convenient to set forth the main experimental results in graphical form. In fig. 2 are recorded the relationships between the gas pressure and the *c/i* values, *i.e.*, cubic centimetres of initial mixture at N.T.P. burnt to H_2O and CO_2 per minute per milliampere, observed at tungsten and gold cathodes respectively, during the cathodic combustion to equilibrium conditions of mixtures of 3 volumes of electrolytic gas diluted with 1, 2 or 3 volumes of carbonic oxide, the range of initial pressures employed being 50 to 110 mm. Fig. 3, in which are recorded changes in the value of *c/i* with the amount of chemical reaction, is typical of the rates of approach to equilibrium observed in our experiments. It will be seen that the rate of combustion was much higher in the absence of sputtered atoms than at a gold cathode. The relationship between the final gas pressure and the equilibrium constant

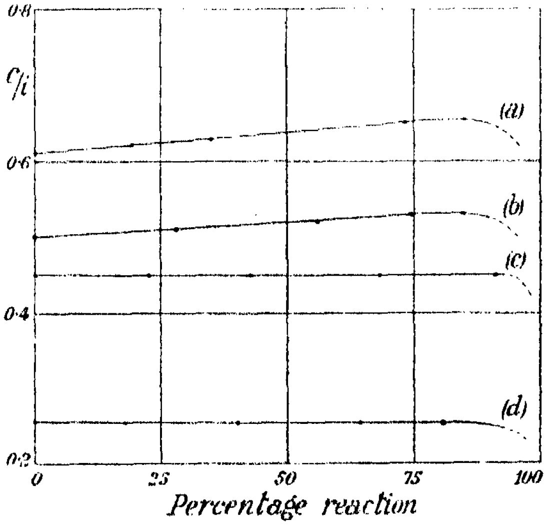

FIG. 3.—(a) $3CO + O_2 + 2H_2 : \overline{W}$, pressure range 85 to 70 mm.; (b) $2CO + O_2 + 2H_2 : \overline{W}$, pressure range 100 to 80 mm.; (c) $CO + O_2 + 2H_2 : \overline{W}$, pressure range 95 to 75 mm.; (d) $2CO + O_2 + 2H_2 : \overline{Au}$, pressure range 60 to 45 mm.

$$K_p = p_{CO} \cdot p_{H_2O}/p_{CO_2} \cdot p_{H_2}$$

is graphically recorded in fig. 4.

Discussion.

The results set forth in fig. 4 establish that, under the conditions of these experiments, the value of the equilibrium constant was independent of the composition of the gas mixture within the limits corresponding to $2H_2O + O_2 + CO$ and $2H_2 + O_2 + 3CO$, a result which is in accordance with the law of mass action. On the other hand, whereas according to this law pressure should likewise be without effect, the observed values of K_p varied continuously with pressure throughout the range examined. This result cannot reasonably be attributed to adsorption of steam on the walls of the reaction vessel because, as pointed out above, the initial CO concentration did not affect the values of K_p. Indeed, the inflection of the curve, fig. 4, to a well-defined minimum must dispose of any such explanation and strongly suggests that the velocity of at least one of the opposing reactions is dependent upon the pressure.

It has been shown previously (Part VI) that the rate of cathodic combustion of CO by steam to CO_2 in moist CO-O_2 mixtures containing excess combustible, is practically independent of the presence or otherwise of sputtered metal atoms, but decreases with increasing gas pressure. These facts led to the view put forward in Parts VI and VII of this series that the cathodic combustion of CO in moist CO-O_2 mixtures could and did take place in two distinct ways and that, whilst an increase in pressure reduced the rate of the one, it favoured that of the other. Thus, according to this view, an increase in pressure reduces the rate of the reaction :—

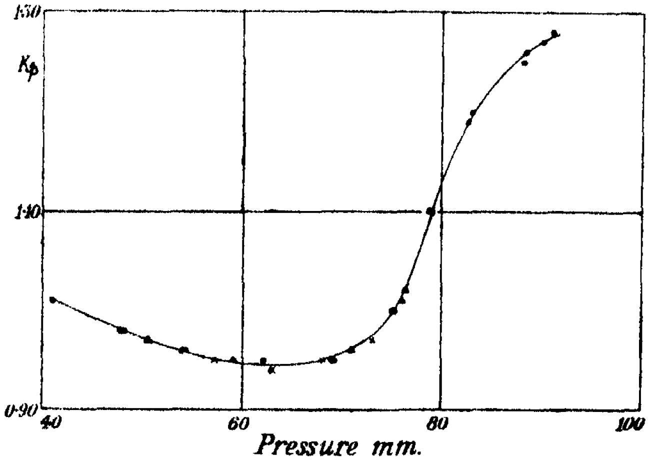

Fig. 4.—△, $3CO + O_2 + 2H_2 : \overline{W}$; ⊙, $2CO + O_2 + 2H_2 : \overline{W}$; ×, $CO + O_2 + 2H_2 : \overline{W}$; □, $2CO + O_2 + 2H_2 : \overline{Au}$.

$$CO + H_2O \rightarrow CO_2 + H_2,$$

but leads to an increase in the rate of the alternative reaction :—

$$2CO + 2OH \rightarrow 2CO_2 + H_2,$$

the necessary supply of OH (or possibly H_2O_2) being furnished partly by the combustion of hydrogen set free in accordance with both the above equations and partly by the direct decomposition of steam by the electric discharge, thus :—

$$2H_2O \rightarrow 2OH + H_2.$$

The fact that for the cathodic water-gas equilibrium K_p varies with the pressure in the manner shown in fig. 4, and in so doing falls to a well-defined minimum value in the neighbourhood of 65 mm., affords strong support of the view outlined above, according to which two alternative lines of approach from the CO side exist, an increase in pressure being favourable to the one but not to the other. Thus the cathodic water-gas equilibrium involves, according to this view, the following cycles of reactions :—

$$\begin{aligned} &\text{(i)} \quad CO_2 + H_2 \rightarrow CO + H_2O \\ &\text{(ii)}\ (a)\ CO + H_2O \rightarrow CO_2 + H_2 \\ &\qquad (b)\ 2CO + 2OH \rightarrow 2CO_2 + H_2. \end{aligned}$$

The results recorded in figs. 2 and 3, in which are shown the rates of cathodic combustion of various $CO\text{-}O_2\text{-}H_2$ mixtures, confirm and extend the results previously set forth in Part VII. They show in particular that the rate of cathodic combustion is independent of pressure, provided the concentration of electrolytic gas in $(2H_2 + O_2)\text{-}CO$ mixtures exceeds 75% by volume.

Summary.

The water-gas equilibrium in the cathode zone of an electric discharge has been investigated. It has been found that the position of equilibrium varies with the final gas pressure. From this and other facts previously established it is concluded that equilibrium is approached from the carbonic oxide side in two ways, pressure being favourable to the one but unfavourable to the other.

The Volume Coefficients of Expansion of Several Gases at Pressures below One Metre.

By J. B. M. Coppock and R. Whytlaw-Gray, F.R.S., Leeds University.

(Received July 26, 1933.)

Introduction.

There have not appeared recently any new determinations of the rate of change of the volume coefficient of expansion of condensable gases at pressures in the neighbourhood of a half to one metre. The work of Henning and Heuse* and Heuse and Otto† has been confined to a study of the permanent gases, their results leading to the conclusion that up to a pressure of 1 metre the rate of change of either the pressure or volume coefficient is a linear function of the pressure. Our knowledge of the behaviour of the condensable gases in this connection rests almost entirely on the very careful work of Chappuis‡, who in 1907 made a series of accurate determinations of the volume coefficients of expansion of carbon dioxide at a series of pressures from 1500 mm. to 500 mm. and over several temperature ranges. The investigation led to one unexpected conclusion which Chappuis left largely unexplained. On linear extrapolation to zero pressure of the graph of pressure against the mean coefficient of expansion over temperature intervals 0–20°, 0–40°, 0–100° C., the limiting value of the coefficient rose from the normal value of 0·003661 for the 0–20° determinations to 0·003671 for those made over the range 0–100° C. Chappuis concludes "that condensation on the reservoir surface plays a part in the irregularities but it is difficult to obtain a satisfactory explanation."

As far back as 1853 Magnus§ demonstrated that the adsorption of sulphur dioxide on glass was sufficient to affect measurements of the expansion coefficients of gases, and the importance of this error was recognized by Chappuis‖ who in 1879 applied a correction to Regnault's measurements. Richards and Mark¶ and Baly and Ramsay** have pointed out the necessity for a knowledge of the amount of adsorption on the walls of the containing vessels when undertaking such determinations.

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* 'Z. Physik,' vol. 5, p. 285, and vol. 6, p. 264 (1921).

† 'Ann. Physik,' vol. 2, p. 1012 (1929).

‡ 'Trav. et Mem. Bur. Int. Poids et Mes.,' vol. 13, p. 93 (1907).

§ 'Ann. Physik,' vol. 89, p. 604 (1853).

‖ 'Ann. Physik,' vol. 8, p. 1 (1879).

¶ 'Proc. Amer. Acad. Arts and Sci.,' vol. 41, p. 117 (1905).

** 'Phil. Mag.,' vol. 38, p. 301 (1894).

Recently Heuse* again showed the effect using neon and helium, for on increasing the surface exposed to the gas sixfold by introducing Jena glass rods into the thermometer bulb, a marked increase in both the volume and pressure coefficients of expansion was produced owing to evolution of surface layers with rise in temperature. The results showed that though the difference between values obtained with and without Jena glass rods in the thermometer bulb for the pressure coefficient remained sensibly constant whatever the initial pressure, the difference between the values of the volume coefficient increased with decrease in pressure. A possible explanation of this effect would be that for the pressure coefficient where measurements are made at constant volume, the excess of pressure caused by evolution of surface layers will remain practically constant whatever the pressure. For the coefficient at constant pressure, though the actual size of the adsorbed layer removed with rise in temperature may remain approximately constant, its volume at any particular pressure will vary inversely as that pressure, hence the effect of adsorption will be greater the lower the pressure. This would account for the abnormal extrapolation to zero pressure of Chappuis' results, and provided the adsorbed layer was not large the linear relationship of pressure to volume coefficient would be obtained.

The work here described is an attempt to elucidate further the problems brought forward in this introduction. Determinations of the volume coefficients of expansion of several gases have been made using both glass and silica reservoirs and evidence of the effect of adsorption on such measurements has been gained.

EXPERIMENTAL.

(a) *The Modified Callendar Thermometer.*

In a series of papers Callendar† described a type of constant pressure air thermometer which he used for the exact determination of temperature, assuming the value of the expansion coefficient of the gas used as the thermometric substance. The method adopted in this work assumes an exact knowledge of the temperature interval, and by use of the Callendar thermometer gives a means of determining the volume coefficient of expansion of any gas. The apparatus is compensated for external temperature changes according to the method adopted by Callendar* in the final form of instrument.

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* 'Z. Physik,' vol. 37, p. 157 (1926).

† 'Phil. Trans.,' A, vol. 178, p. 223 (1887); Callendar and Griffith, vol. 182, p. 119 (1891).

The pressure of the gas enclosed in the thermometer bulb T, fig. 1, is constantly maintained at the same standard pressure as that of the gas in another bulb S kept at constant pressure. Equality of pressure is indicated by the gauge G. Thus if the temperatures of T, S and M are initially adjusted to equality, and then the gas in T is heated (S and M being kept at the initial temperature), in order to maintain constant pressure in the apparatus mercury must be withdrawn from M, and the quantity collected represents the expansion of the gas initially contained in the bulb T.

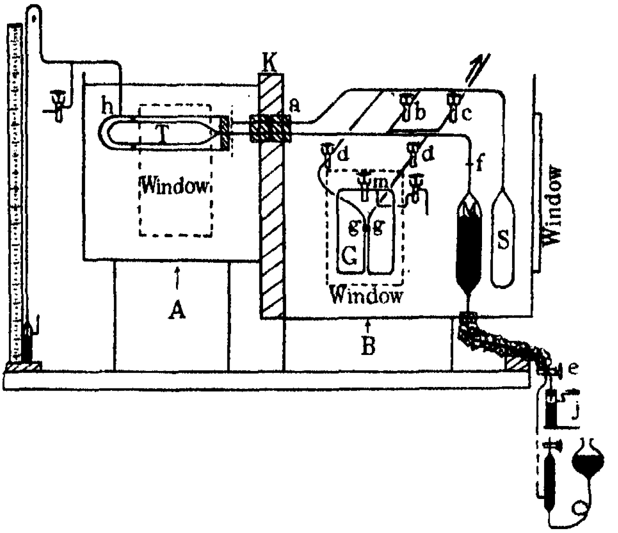

FIG. 1.

The experiments here described have been made over two distinct temperature ranges, namely, 25° to 50° C. termed the "First Series" and 11° to 48° C. designated the "Second Series." Modification of the apparatus used in the first series of determinations was made so as to work at a lower initial temperature in the second series, other slight modifications were also made and these will be described where necessary.

The bulb T, in which the gas whose expansion coefficient is required is heated, is contained in the tank A. This bulb is connected to a second one M by means of a capillary tube 1·5 mm. bore passing through rubber bungs inserted in the tank side at *a*. A second capillary tube enters the tank A through the bungs and is adjusted so that its volume is very nearly equal to the volume occupied by the capillary joining the calibration mark on T to the point *a*. Equality of volume is obtained by calibration with mercury. This method has been adopted for determining the volume of the connecting tubes on the "expansion" side of the apparatus, filling the tubes required for constructing the "compensation" side with the same volume of mercury and using this length of tube for the construction. As the two sets of tubing are of the same diameter they have equal surfaces, they are therefore not only compensated for external temperature changes, but also for adsorption on the walls of the tubing.

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* 'Proc. Roy. Soc.,' A, vol. 50, p. 247 (1891).

At the lower end of the bulb M a capillary tube passes through a bung in the base of the tank B to a three-way tap *e*. By means of this tap the bulb M may either be filled with mercury up to the mark *f* (which is the point where equality of volume in the compensation and expansion part of the apparatus is obtained), or mercury may be withdrawn into the tared vessel *j* which may be partially evacuated when the head of mercury from *f* to *j* is insufficient to effect passage through the tap nozzle. A T-piece connects this half of the system to the gauge G by way of a tap *d* and ground glass joint *g*. The other part of the system is the compensating side and consists of the sealed-off capillary tube previously mentioned passing from the tank A to the bulb S. A T-piece connects this part of the apparatus by way of a tap to the gauge, a second T-piece connecting the expansion side to the compensating side through the tap *b*. This tap allows the bulb S to be filled with the required gas and then isolated from the expansion side of the apparatus after equalization of pressure on both sides of the gauge.

As the whole apparatus must be immersed in water at constant temperature so as to obtain reproducible results mercury sealed taps are used throughout; having closed bases they may be adjusted so that the water just covers the connecting capillaries, allowing the whole of the apparatus in tank B to be maintained at constant temperature.

The tap *c* leads to a manometer and thence by way of a T-piece and tap to a drying train and liquid air trap, through which the gases are introduced into the Callendar thermometer. The pressure of the gas in the thermometer is read on the differential manometer when the tanks A and B are maintained at the initial temperature. If the mercury height in the reservoir M is adjusted to the mark *f*, the pressure measured is the value of the constant pressure at which determinations of the volume coefficient are made. Hence after a value has been determined by raising the temperature of the bulb T and running out mercury, on cooling the system to the original temperature and re-adjusting the mercury to the mark *f*, the same pressure prevails, allowing any number of determinations to be made at one pressure.

The Gauge.—The accuracy of the results is to a large part dependent on the response of the gauge liquid to small pressure differences. An ordinary U type of gauge was modified to meet the demands of the method. It was necessary that the gauge could be (*a*) totally immersed in the constant temperature bath ; (*b*) easily removable so as to replace the gauge liquid after use with any one gas ; (*c*) prevented from responding to pressure differences large enough to blow the liquid into the thermometer ; and (*d*) filled *in situ* with freshly evacuated oil after the gas had already been introduced into the Callendar thermometer owing to the impossibility of evacuating the oil whilst in the gauge.

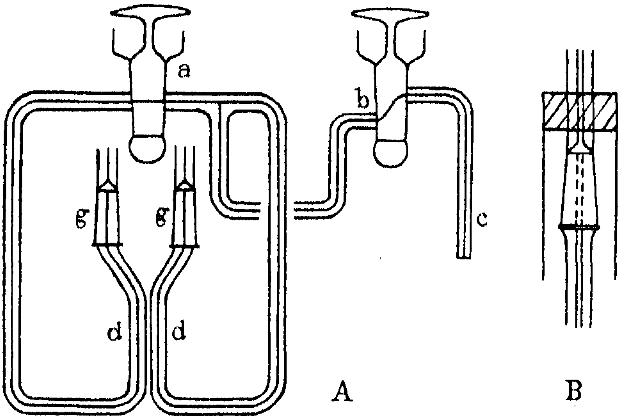

Fig. 2.

Fig. 2 A shows the form of gauge adopted, it being constructed from 2 mm. capillary tubing throughout. The connections to the Callendar thermometer are made by ground glass joints *g*, protected from contact with water by a diving bell device illustrated in fig. 2 B. The limbs *dd*, are constructed as close together as possible so that they may be observed through the same field of vision when viewed through a telescope some feet away. The introduction of the gauge liquid is made through the tap *b* as described hereafter. Before insertion of the gauge into the ground joints the limb *c* is filled with mercury to the point *b*. After placing in position the gauge is evacuated together with the Callendar thermometer and finally filled with the gas under investigation. A tube containing the gauge liquid is then placed so that the limb *c* is totally immersed, the pressure in the apparatus is increased slightly above atmospheric, the tap *b* opened and the mercury blown out into the bottom of the tube. The

pressure is then reduced and the oil rises into the limbs of the gauge. After filling to the required point mercury is again drawn into the tap *b* so as to seal the apparatus from air or water leaks caused by solution of the tap grease in the gauge liquid. The tap *a* isolates the two sides of the gauge so that pressures may be equalized without danger of the liquid flowing into the expansion reservoirs. It will be observed that it would be impossible for air to enter the apparatus during the filling of the gauge by this method.

The Gauge Liquid.—In the original Callendar thermometer sulphuric acid was used as the gauge liquid. Owing to the acid possessing an appreciable vapour pressure at room temperature it was replaced by n. dibutyl phthalate which responds readily to small pressure changes and has an extremely small vapour pressure. Hickman and Sanford* give v.p. $= 7 \cdot 8 \times 10^{-5}$ mm., and Zabel† $4 \cdot 2 \times 10^{-5}$ mm. at 25°C. The ester was evacuated for at least 3 hours before use in order to remove dissolved air. The level of the gauge liquid was read by means of a telescope fitted with crosswires, illumination was effected by transmitted light passing through the tank window and reflected by a milk glass screen situated behind the gauge.

The Temperature Control.—The Callendar conditions stipulate that for perfect compensation the initial temperatures of the three bulbs S, T and M, fig. 1, must be the same, thus the temperature of the water in the tanks A and B must be initially thermostatted to exact equality. The temperatures were controlled to within 0·01° C. by use of thermoregulators, relays, heaters and stirrers as designed by Hume,‡ with slight modifications of the two regulators in the bath A so as to facilitate control of the two temperatures at which the bath is worked.

The temperatures were read on thermometers calibrated against a very recently obtained National Physical Laboratory standard, and were known to within ± 0·01° C. They were periodically checked against the standard. Determinations were made with reference to etched markings on the thermometers only, slight adjustment of the thermoregulators always reproducing the working temperature any number of times. The temperatures given in the tables of results have been corrected to the N.P.L. values [International Temperature Scale].

Further Details.—In the first series of experiments the working temperatures of 25° to 50° C. were easy to maintain, but in the second series it was decided to work at a lower initial temperature and over a greater range.

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* 'J. Phys. Chem.,' vol. 34, p. 637 (1930).

† 'Rev. Sci. Inst.,' vol. 4, p. 233 (1933).

‡ 'J. Opt. Soc. Amer.,' vol. 19, p. 158 (1929).

An Electrolux refrigerator unit, Type 100, extracting 400 B.T.U. per hour was considered to have sufficient capacity to keep the temperature of the baths initially at 10° C. and subsequently maintain the larger tank B at this temperature whilst A was heated to 50° C. Satisfactory control to 0·01° C. was only possible when working between 11° and 48° C. A large volume of water was cooled in an insulated tank and was circulated by means of an electrically propelled gear pump through lead "compo" cooling coils, supported on 1-inch angle iron strips mounted on the bases of the tanks A and B. Suitable cork lagging was used on the tank sides to prevent temperature fluctuations. The cooling coils were connected in parallel to the gear pump by means of ¾-inch rubber tubing lagged with plumber's felt. Clips on these tubes allow either one or both coils to be supplied with cold water from the cooling unit, so that the tanks may be run simultaneously at the same temperature or the larger tank kept at the lower temperature whilst that of A is elevated.

The Callendar thermometer used in the second series was unaltered from that in previous use except for one detail. The additional feature was a pressure equalizer *h*, fig. 1, with which the pressure of air outside the expansion reservoir T could be made equal to that of the gas contained within, hence no distortion of the bulb due to inequality of pressure on both sides of it should occur. On comparing coefficients at 400 mm. it was found immaterial whether the equalizer pressure was 400 mm. or 760 mm., so that no error due to distortion of the bulb occurred in the first series of experiments.

On original construction the whole apparatus was carefully cleansed and dried. The mercury used in the bulb M was washed with a solution containing mercurous nitrate and nitric acid, dried, filtered and distilled *in vacuo*, its purity was certainly high.

(*b*) *The Course of an Experiment.*

It will be convenient to describe the method of working assuming the Callendar thermometer has previously been used for a determination of the volume coefficient of some gas. This will show the method adopted to remove traces of easily adsorbable gases before new work is commenced.

Previous to the introduction of the gas into the Callendar thermometer complete evacuation to 0·01 mm. is effected. The bulb T is maintained at the higher working temperature to remove layers that are evolved on rise of temperature. The whole apparatus is then completely washed out several times with CO_2-free air, the gauge undergoing the same treatment before introduction of the dibutyl phthalate. After further evacuation the gas is solidified in a liquid air trap, pumped down and allowed to volatilize slowly, the middle fraction being passed into the Callendar thermometer. After the filling of the gauge the pressure is reduced to the lowest working value, and the mercury in M adjusted to the mark f after the temperatures of the two tanks have been made equal. The time given for the gas to maintain equilibrium with the gauge liquid is 48 hours after which the pressure is read on the manometer. The tap c is then closed and a determination of the volume coefficient may be made. It is assumed that at this stage the taps b, d and m are all open and the pressure is constant throughout the system, as indicated by the level of the gauge liquid. When making further determinations at this pressure the apparatus is maintained in this condition for at least 3 hours to allow the full restoration of temperature equilibrium. The tap b isolating the compensation from the expanson side is then closed, the surfaces of the gauge liquid remaining quite level if the temperature control is to within 0·01° C. The gauge is now isolated from the system by closing the taps d, the heating of the gas being effected by switching over to the high temperature thermoregulated circuit. The heating takes about 3 hours and the bulb T is maintained at the higher temperature for an hour to obtain temperature equilibrium. Mercury is now withdrawn from the reservoir M by way of the tap e into the tared vessel j. The volume of mercury required to attain approximate equality of pressure on both sides of the gauge is determined by a trial run. This volume is run out, the taps d opened, and final adjustment of the gauge level made by careful withdrawal of mercury until equality of pressure is exactly indicated. This procedure serves two purposes. In the first place the capillary joining e to the tanks, though lagged with cotton wool, is exposed to room temperature, and it is necessary that the final withdrawal of mercury should not be completed before the tube has again reached room temperature. Secondly, as the pressure on both sides of the gauge is kept nearly constant, differential evolution of gas will not occur thus eliminating this possible source of error. The mercury is then weighed and from this the value of the volume coefficient of expansion of the gas calculated.

(c) *Calculation of Results.*

(1) *The coefficient* $\alpha_{t_2 \rightarrow \mathrm{T}}$ *referred to the volume of gas* t_2° C.—Let

w = weight of mercury run out from M to obtain constancy in pressure.

f_{t_1} = conversion factor gram of mercury to cubic centimetre at the temperature of the tank containing M. (t_1).

$\alpha_{t_2 \rightarrow \mathrm{T}}$ = coefficient of expansion of the gas from $t_2°$ to T° C.
$t_2°$ C. = the initial temperature of the gas in the bulb T.
T° C. = the final temperature of the gas in the bulb T.
$t_1°$ C. = the temperature of the bulb M.
V = the volume in cubic centimetres of gas contained in the expansion bulb at $t_2°$ C.
β = coefficient of cubical expansion of the bulb material.

Then it may be shown that

$$\alpha_{t_2 \rightarrow \mathrm{T}} = \frac{wf_{t_1} + \mathrm{V}_\beta [\mathrm{T} - t_2]}{\mathrm{V} [\mathrm{T} - t_2] - wf_{t_1} [\mathrm{T} - t_1]}, \tag{1}$$

and if the Callendar conditions are exactly fulfilled $t_1 = t_2$ and f_{t_1} becomes f_{t_2}, hence

$$\alpha_{t_2 \rightarrow \mathrm{T}} = \frac{wf_{t_2} + \mathrm{V}_\beta [\mathrm{T} - t_2]}{\mathrm{V} [\mathrm{T} - t_2] - wf_{t_2} [\mathrm{T} - t_2]}. \tag{2}$$

(2) *The Value of the Volume Coefficient of Expansion of the Gas when referred to the normal scale of the volume of the gas at* 0° *C.*—Let this value be $\alpha^\circ_{t_2 \rightarrow \mathrm{T}}$ and let V_0 be the volume of the gas at 0° C., α_{t_2} the coefficient of expansion of the gas from 0° to $t_2°$ C.

Then we may write

$$\alpha_{t_2 \rightarrow \mathrm{T}} = \frac{[\mathrm{V}_0 + \mathrm{V}_0 t_2 \alpha_{t_2} + \mathrm{V}_0 (\mathrm{T} - t_2)\, \alpha^\circ_{t_2 \rightarrow \mathrm{T}}] - [\mathrm{V}_0 + \mathrm{V}_0 t_2 \alpha_{t_2}]}{[\mathrm{V}_0 + \mathrm{V}_0 t_2 \alpha_{t_2}] [\mathrm{T} - t_2]}$$

for

$$\alpha_{t_2 \rightarrow \mathrm{T}} = \frac{(\text{vol. of gas at T° C.}) - (\text{vol. of gas at } t_2° \text{ C.})}{(\text{vol. of gas at } t_2° \text{ C.})\ (\mathrm{T} - t_2)}.$$

Hence

$$\alpha^\circ_{t_2 \rightarrow \mathrm{T}} = \alpha_{t_2 \rightarrow \mathrm{T}} [1 + t_2 \alpha_{t_2}]. \tag{3}$$

Now for the permanent gases $d\alpha/dt$ is small and $\alpha_{t_2} = \alpha^\circ_{t_2 \rightarrow \mathrm{T}}$.

Therefore

$$\alpha^\circ_{t_2 \rightarrow \mathrm{T}} = \frac{\alpha_{t_2 \rightarrow \mathrm{T}}}{1 - t_2 \alpha_{t_2 \rightarrow \mathrm{T}}}. \tag{4}$$

But for the compressible gases $d\alpha/dt$ is not small and equation (4) is not strictly true. In order to calculate true values of $\alpha^\circ_{t_2 \rightarrow \mathrm{T}}$ correct to 1 part in 4000, values of α_{t_2} must be known to within about 1 part in 600. This may be obtained from the value of $\alpha^\circ_{t_2 \rightarrow \mathrm{T}}$ calculated approximately from equation (4) as follows.

It is well known that α decreases with increase in temperature, hence $\alpha_{t_1} > \alpha^{\circ}_{t_1 \to \mathrm{T}}$. Further it may be shown from Leduc's* calculations that the difference between two coefficients, say $\alpha_{0 \to 25} - \alpha_{0 \to 75}$ is a linear function of the coefficient $\alpha_{0 \to 75}$, the greater the divergence of α from 0·003661 the larger the difference. It has also been shown by Chappuis (*loc. cit.*) that the rate of change of coefficient is linear and the results here obtained support that view. Thus we have

$$k_1 p = [\alpha^{\circ}_{t_1 \to \mathrm{T}} - \alpha_{\text{limiting}}]$$
$$k_2 \Delta = [\alpha^{\circ}_{t_1 \to \mathrm{T}} - \alpha_{\text{limiting}}],$$

where $\Delta = \alpha_{t_1} - \alpha^{\circ}_{t_1 \to \mathrm{T}}$, p the pressure in millimetres and α_{limiting} the value of α at zero pressure. k_1 and k_2 are constants.

Hence $\Delta = \mathrm{K}[\alpha^{\circ}_{t_1 \to \mathrm{T}} - \alpha_{\text{limiting}}] \cdot p$, where K is a constant. Theoretically $\Delta = 0$ when $p = 0$, but owing to adsorption phenomena probably making Δ smaller than it should be theoretically we find from Chappuis' results that $\Delta = 0$ when $p = 300$ mm.

Thus our equation becomes :—

$$\Delta = \mathrm{K}[\alpha^{\circ}_{t_1 \to \mathrm{T}} - \alpha_{\text{limiting}}][p - 300]. \tag{5}$$

Therefore Δ, the difference between α_{t_1} and $\alpha^{\circ}_{t_1 \to \mathrm{T}}$ may be calculated over a range of pressures and values of α.

Chappuis has shown that α is a linear function of the temperature interval and it may be shown that $\alpha_{25 \to 50} = \alpha_{0 \to 75}$ and $\alpha^{\circ}_{11 \to 48} = \alpha_{0 \to 60}$. The proof may be obtained by use of the Beattie-Bridgeman equation of state as previously developed by one of us,† *e.g.*, for CO_2 at 760 mm.

$$10^6 \alpha^{\circ}_{11 \to 48} = 3727 \qquad 10^6 \alpha_{0 \to 60} = 3727.$$

From Chappuis' results we find that $10^6 \alpha_{0\text{-}25} - 10^6 \alpha_{0\text{-}75} = 8$ and $10^6 \alpha_{0\text{-}11} - 10^6 \alpha_{0\text{-}60} = 7$, at 800 mm. where $10^6 \alpha_{0\text{-}75} = 3730$ and $10^6 \alpha_{0\text{-}60} = 3733$. These are taken as standard values from which K may be obtained, and hence values of Δ for any pressure below 800 mm. and a maximum of $10^5 \alpha = 374$ may be calculated therefrom. The corrections applied to dimethyl ether are of necessity large and are estimated from Leduc's calculations.

Hence from equation (5) we find values of Δ to be added to the approximate value of $\alpha^{\circ}_{t_1 \to \mathrm{T}}$ calculated from equation (4) in order to give values of α_{t_1}.

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* 'Ann. physique,' vol. 5, p. 180 (1916).

† Coppock, 'J. Phys. Chem.' (*in the press*).

The corrected value of $\alpha^\circ_{t_2\rightarrow T}$ is then calculated from equation (3) using the value of α_{t_2} as determined above, the final equation becoming

$$\alpha^\circ_{t_2\rightarrow T\ \text{corrected}} = \alpha_{t_1\rightarrow T}\,[1 + t_2\,(\alpha^\circ_{t_2\rightarrow T\ \text{uncorrected}} + \Delta)].$$

(*d*) *Preparation of Gases.*

(1) *Ethylene.*—Pure ethylene was prepared from ethyl alcohol and syrupy phosphoric acid, bubbled through potash solution, and subsequently passed several times over phosphorus pentoxide. The gas was solidified, traces of air pumped off, fractionated and the middle fraction collected for use.

(2) *Air, free from Carbon Dioxide.*—The air was purified from carbon dioxide, etc., by bubbling through 50% potash, dried over concentrated sulphuric acid and phosphorus pentoxide.

(3) *Carbon Dioxide.*—The carbon dioxide was prepared by heating sodium bicarbonate *in vacuo*, passing the water and CO_2 formed over metaphosphoric acid, further dried over phosphorus pentoxide, solidified, air pumped off and fractionated, the middle fraction being collected.

(4) *Nitrous Oxide.*—Nitrous oxide was prepared by dropping a solution of sodium nitrite into a concentrated solution of hydroxylamine hydrochloride. A slight brown colour of nitrogen peroxide developed on standing, 3 litres of gas were prepared, mixed with 20 c.c. oxygen to oxidize nitric oxide to the peroxide, this was removed by bubbling through 50% potash, the gas was dried over phosphorus pentoxide, solidified, the excess oxygen pumped off. fractionated and the middle fraction collected.

(5) *Dimethyl Ether.*—The gas was synthesized from sodium methoxide and methyl iodide. The ether was passed by way of a reflux to a U-tube packed with glass wool and cooled in ice, passed several times over anhydrous calcium chloride and freshly prepared quicklime, solidified in liquid air, air pumped off and fractionated. The gas was dried over quicklime before introduction into the Callendar thermometer and not over pentoxide as was the usual procedure.*

(6) *Nitric Oxide.*—Equimolecular quantities of potassium ferrocyanide and potassium nitrite were dropped into dilute acetic acid and the nitric oxide collected over water in a gas holder. The reservoir was then connected to an all-glass apparatus that had been completely evacuated, the nitric oxide passed over metaphosphoric acid, bubbled through concentrated sulphuric acid, solidified, pumped free from non-condensable gases and fractionated.

(7) *Carbon Monoxide.*—Carbon monoxide was prepared *in vacuo* from formic and sulphuric acids previously degassed, passed over solid potash, phosphorus

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* Cawood and Patterson, 'J. Chem. Soc.,' p. 619 (1933).

pentoxide and through a spiral cooled in liquid air to remove condensable gases.

(8) *Sulphur Hexafluoride.*—The authors are greatly indebted to Mr. K. G. Denbigh, B.Sc., for preparing them a sample of pure sulphur hexafluoride. Fluorine was passed through a copper tube containing sodium fluoride to remove hydrogen fluoride and then through a second tube containing recrystallized sulphur. The hexafluoride formed was bubbled through potash, solidified, and collected in Winchesters over potash and allowed to stand for some weeks. The gas was then fractionated after air had been pumped off until a sample of constant density was obtained as determined with a microbalance. Contamination with SO_2F_2 was suspected and after passage over sodium and potassium liquid alloy density determinations showed the gas to be between 99·4% and 99·8% pure.

(*e*) *Results.*

In view of the large number of determinations made considerable condensation has been necessary, complete results are given, however, for carbon dioxide in the second series so as to show the accuracy of the method adopted. N represents the number of determinations made.

Table I.

p in mm.	t_1.	t_2.	T.	Mean w.	N.	$10^8\, a_{t_1 \to T}$.	$10^8\, a^{\circ}_{t_1 \to T}$ uncorrected.	$10^7\, a^{\circ}_{t_1 \to T}$ corrected.
				Ethylene.				
454	24·97	25·01	50·01	115·586	6	339201	37064_4	3706_8
644	24·97	25·01	50·01	116·072	4	340739	37248_2	3725_1
780	25·01	25·01	50·01	116·391	6	341697	37362_6	3737_0
				Carbon dioxide.				
411	25·01	25·01	50·01	115·403	7	338682	36990_5	3699_1
610	25·01	25·01	50·01	115·799	7	339830	37139_5	3714_4
773	25·01	25·01	50·01	116·138	8	340902	37267_6	3727_4
				Nitrous oxide.				
429	25·01	25·01	50·01	115·492	7	338864	37024_2	3702_6
607	25·01	25·01	50·01	115·876	7	340070	37168_3	3717_3
781	25·01	25·01	50·01	116·279	7	341346	37320_6	3732_8
				Air, CO_2-free.				
411	25·01	25·01	50·01	114·564	5	335938	36674_8	3667_8
551	25·01	25·01	50·01	114·635	5	336160	36701_7	3670_3
759	25·01	25·01	50·01	114·686	5	336324	36721_2	3672_3

First Series. Determinations made between 25° and 50° C.

Volume of expansion bulb T1 at 25·01° C. = 110·205 c.c. Bulb material—soft glass. Surface area of bulb = 150 sq. cm. Volume of compensation bulb S1 at 25·01° C. = 110·22 c.c. Coefficient of cubical expansion of bulb material as determined by weight thermometer measurements = 0·0000289.

Table II.—Carbon dioxide.

p in mm.	t_1.	t_2.	T.	w.	Mean of $10^8\,\alpha_{t_1\rightarrow T}$.	$10^8\,\alpha^{\circ}_{t_1\rightarrow T}$ uncorrected.	$10^7\,\alpha^{\circ}_{t_1\rightarrow T}$ corrected.
(a) Results with glass reservoir T2.							
425	11·03	11·03	48·01	231·938 232·015 232·010 231·948 231·970 232·010	355644	37016_4	3701_7
590	11·03	11·03	48·01	232·700 232·691 232·654 232·647 232·684 232·697	356844	37145_7	3714_8
792	11·03	11·03	48·01	233·465 233·492 233·521 233·502 233·514 233·531	358263	37300_8	3730_3
(b) Results with silica reservoir T3.							
394	11·03	11·03	48·01	249·765 249·754 249·730 249·758 249·790 249·758	354993	36946_0	3694_6
600	11·03	11·03	48·01	250·728 250·708 250·743 250·710 250·733 250·691	356535	37113_0	3711_4
784	11·03	11·03	48·01	251·637 251·643 251·598 251·619 251·605 251·613	357985	37270_8	3727_3

In the results with ethylene it will be noticed that t_1 and t_2 are not adjusted to equality in the first two lines, this has been taken into consideration in the calculation of the expansion coefficients and equation (1) has been used.

Table III.—Results with silica reservoir T3.

p in mm.	t_1.	t_2.	T.	Mean w.	N.	$10^6\, a_{t_2\to T}$.	$10^8\, a^\circ_{t_2\to T}$ uncorrected.	$10^7\, a^\circ_{t_2\to T}$ corrected.
				Dimethyl ether.				
387	11·03	11·03	48·01	255·206	7	363771	36897_8	3790_9
608	11·03	11·03	48·01	259·497	6	370720	38648_5	3866_9
764	11·03	11·03	48·01	262·585	6	375742	39198_3	3922_0
				Nitric oxide.				
408	11·03	11·03	48·01	248·410	5	352826	36711_8	3671_2
618	11·03	11·03	48·01	248·695	4	353284	36760_9	3676_1
784	11·03	11·03	48·01	248·908	5	353625	36797_9	3679_8
				Carbon monoxide.				
413	11·03	11·03	48·01	248·309	6	352665	36693_8	3669_4
768	11·03	11·03	48·01	248·595	6	353120	36743_1	3674_4
				Sulphur hexafluoride.				
409	11·03	11·03	48·01	252·453	5	359329	37415_7	3741_7
596	11·03	11·03	48·01	254·395	4	362461	37755_5	3775_8
769	11·03	11·03	48·01	256·325	5	365580	38094_1	3810_0

Second series. Determinations made betewen 11° *and* 48° *C.*

(*a*) Volume of glass expansion bulb T2 at 11·03° C. = 148·311 c.c. Bulb material—soft glass from the same length of tubing as used in the first series. Surface area = 180 sq. cm. Volume of compensating bulb S2 at 11·03° C. = 148·31 c.c.

(*b*) Volume of silica expansion bulb T3 at 11·03° C. = 158·725 c.c. Bulb material—fused silica. Surface area = 230 sq. cm. Volume of glass compensation bulb S3 at 11·03° C. = 158·73 c.c.

The silica bulb included a silica to soft glass graded seal having a volume of about 8 c.c. this necessitated the determination of the coefficient of cubical expansion of the bulb as a whole using it as a weight thermometer. A mean value of 0·0000020 was obtained.

Before use the silica bulb was baked to 200° C. in an electric furnace for 6 hours whilst maintained at a high vacuum.

(*f*) *Discussion of Results.*

(*a*) *First series.*—The value of $10^6 \alpha^\circ_{25\rightarrow 50}$ for CO_2-free air at 760 mm. is 3672 which is identical with the accepted experimental figure, and compares favourably with the theoretical value 3671 calculated from the Beattie equation (*loc. cit.*). On linear extrapolation the limiting value α_p at zero pressure is 3662, the true value should be 3661.

No previous value has been obtained for ethylene. At 760 mm. the figure 3736 is obtained, Leduc gives $10^6 \alpha_{0-75} = 3740$ and the Beattie equation 3726. The linear extrapolation to zero pressure does not proceed normally and gives $\alpha_p = 3665$.

Regnault* obtained a value for nitrous oxide $10^6 \alpha_{0-100} = 3720$ at 760 mm., and Jolly† 3708 at 1000 mm., the latter value is undoubtedly low. The value of $10^6 \alpha^\circ_{25\rightarrow 50}$ here determined is 3731, Leduc calculates $10^6 \alpha_{0-75} = 3738$, but as has been pointed out by Langmuir‡ the value should be quite close to that of carbon dioxide, the figure here determined is 0·2% higher. The extrapolation to zero pressure is again abnormal giving $\alpha_p = 3666$.

Considerable data has been accumulated for carbon dioxide by Chappuis. The value here determined compares favourably with experimental and theoretical values :—

Leduc α_{0-75},	Beattie α_{0-75},	Chappuis α_{0-75},	$10^6 \alpha^\circ_{25-50}$ found
3729	3724	3728	3726

It is noteworthy that the non-extrapolation of α values to 3661 at zero pressure observed by Chappuis was again found in this work, the actual value of α_p being 3667.

In the introduction the effect of adsorption on values of α has been discussed briefly. It is here suggested that the non-extrapolation to 3661 at zero pressure is due to this cause. Moles and his co-workers§ have shown the magnitude of adsorption of various gases to be in the order $CO_2 > N_2O > C_2H_4 >$ air, which is precisely the order in which our values of α_p approach the true limiting value. It has also been pointed out that the lower the pressure, the greater is the effect of the evolved surface layers on values of α, thus leading to an extrapolation of the $\alpha - p$ curve to a point higher than the true limiting value.

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* 'Ann. chim. phys.,' vol. 4, p. 5; vol. 5, p. 52 (1842).

† 'Ann. Physik Judelband,' vol. 82 (1874).

‡ 'J. Amer. Chem. Soc.,' vol. 41, pp. 868, 1543 (1919).

§ 'Anal. Phys. Quim.,' vol. 24, p. 210 (1926); vol. 23, p. 223 (1925); vol. 27, p. 529 (1929); vol. 28, p. 448 (1930); vol. 30, p. 520 (1932).

This was thought to be the case particularly with CO_2 and it was considered that elucidation of this effect would be of great interest.

The Effect of Adsorption.—In order to demonstrate quantitatively the effect of adsorption comparison was made of the rate of change of coefficient with pressure for carbon dioxide using expansion reservoirs of different materials, but maintaining the temperature intervals the same in the two series of experiments. The amount of adsorption occurring on plane silica surfaces has been investigated by Clulow* who obtained evidence of the non-formation of layers of CO_2 molecules on such a surface. It was thought, therefore, that a comparison of coefficients using silica and glass vessels would lead to useful information.

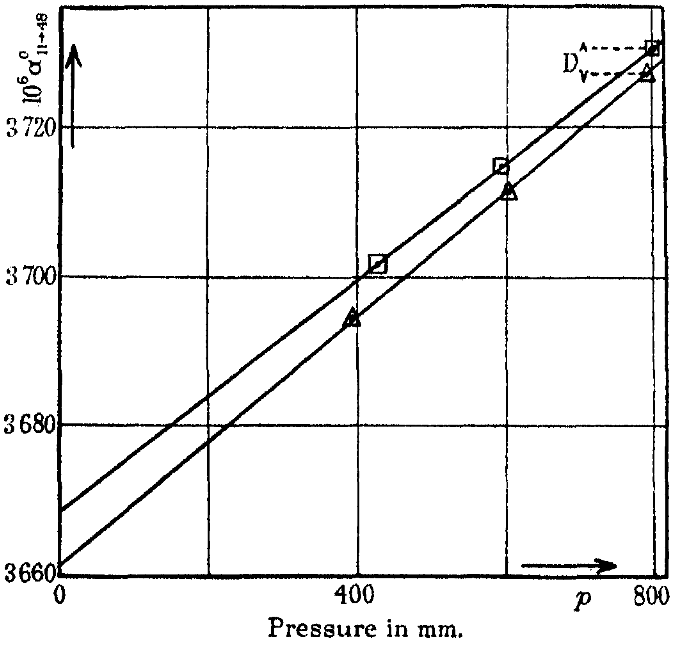

Fig. 3.—⊡ value using glass reservoir; △ value using silica reservoir.

The results are quoted fully in Table II and fig. 3 clearly shows the differences found in the values of the coefficients. The limiting value of $10^6\, \alpha^\circ_{11\to48}$ when using the glass vessel is 3668, far removed from the value 3661 obtained with the silica vessel. It appears that with glass surfaces considerable evolution of surface layers of CO_2 molecules occurs between 11° and 48° C., whereas silica surfaces lead to normal results. From these results the volume of the adsorbed layer may be calculated and a correction applied to series one to give true values unaffected by adsorption phenomena.

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* Ph.D. Thesis, Leeds (1932).

Let

D = the difference between the coefficients at pressure p, fig. 3.

α = the expansion coefficient of the gas in the glass vessel at the pressure p.

V = the volume of the vessel in cubic centimetres.

A = the surface area of the vessel in square centimetres.

Then it may be shown that for corresponding p and α values the volume of the layer evolved per square centimetre of apparent surface at N.T.P.

$$= \frac{\mathrm{D} \, . \, \mathrm{V}t_2 \, . \, p \, . \, 273}{760 \, . \, \mathrm{A} \, . \, [273 + \mathrm{T}]} . \qquad (6)$$

Substituting values of D in the equation we find the volume of CO_2 molecules removed is approximately 7 × 10^{-5} c.c./sq. cm., a monomolecular layer with hexagonal close packing would occupy 3·7 × 10^{-5} cc./sq. cm. Chappuis (*loc. cit.*) found the layer evolved between 0° and 180° C. to be 10·2 × 10^{-5} c.c./sq. cm. and Evans and George* find the layer to occupy 11·5 × 10^{-5} c.c./sq. cm., the value here determined appears to be of the correct order of magnitude.

Correction to the First Series.—From these data corrections may be applied to values of $10^6 \alpha^{\circ}{}_{25 \rightarrow 50}$ for nitrous oxide and ethylene. The diameters of the molecules as given by Landolt and Bornstein are approximately the same, and from Moles and his co-workers results (*loc. cit.*) we may write the relative volumes of the adsorbed layers in the order $1_{CO_2} : 2/3_{N_2O} : 1/3_{C_2H_4}$. Here the temperature range is two-thirds that of the 11° to 48° C. measurements made for CO_2 above, and the correction to the 25° to 50° C. values assumes 4·0 × 10^{-5} c.c./sq. cm. of CO_2 to be evolved between these two temperatures. The following corrections are calculated from equation (6).

On plotting the values of α obtained after deduction of these corrections against pressure the limiting values lie between 3660 for carbon dioxide and

Table IV.—Corrections to be applied at various pressures × 10^6.

p = 760 mm.	600 mm.	400 mm.
CO_2 . 2·6	2·4	4·9
N_2O . 1·8	3·2	3·3
C_2H_4 . 0·9	1·1	1·6

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* 'Proc. Roy. Soc.,' A, vol. 103, p. 190 (1923).

3662 for ethylene The corrected values at 760 mm. give for CO_2 $10^6\,\alpha^\circ_{25\rightarrow50} =$ 3723 (compare the Beattie value 3724), for N_2O 3729, and for C_2H_4 3735.

Second Series.—Leduc's calculations predict a value $10^5\,\alpha_{0-60} = 3940$ for dimethyl ether, the value actually found is $10^6\,\alpha^\circ_{11\rightarrow48} = 3920$ at 760 mm. The extrapolation to zero pressure is low (3658) but with a gas of this type $d\alpha/dp$ may not be linear. It appears, however, that the values are little affected by adsorption at 400 mm. giving additional proof of the reliability of silica vessels in such determinations.

For nitric oxide no previous data are available except that calculated by Leduc, his value is $10^6\,\alpha_{0-60} = 3675$ at 760 mm., whereas the experimental figure of 3679 is rather higher.

Regnault made the only determination of α for carbon monoxide and obtained $10^6\,\alpha_{0-100} = 3669$ at 760 mm., the result is probably low and would be expected to lie closer to the oxygen and nitrogen values. The value here determined is $10^6\,\alpha^\circ_{11\rightarrow48} = 3674$ at 760 mm. which compares well with Leduc's figure $10^6\,\alpha_{0-60} = 3673$. The corresponding values for nitrogen and oxygen as calculated from the Beattie equation are 3672 and 3674 respectively.

As the critical points of sulphur hexafluoride and hydrogen sulphide are in near proximity their coefficients should resemble one another. The value for SF_6 here found is 3808 at 760 mm., the corresponding value for H_2S as calculated by Leduc being 3790.

It is thought desirable from a consideration of these results to emphasize the importance of using some *standard material* for measurements of the expansion coefficients of the more easily condensable gases. The differences found in the values of the coefficients as determined by different workers are probably to a large extent dependent on the nature of the material used for the construction of the expansion reservoirs. It appears that with silica vessels values of the volume coefficient of expansion for the easily condensable gases may be obtained with little fear of errors occurring owing to adsorption phenomena, and before comparable results can be obtained with such gases materials must be used that are not subject to adsorption effects. The suggestion is advanced that *fused silica* would be the most advisable material to adopt as standard.

Summary of Results.

The following values of the volume coefficients of expansion at 760 mm. have been interpolated from the data obtained with various gases over an approximate pressure range of a half to one atmosphere.

Values of the volume coefficient of expansion at 760 mm.

Gas.	$10^6\,\alpha^\circ_{25\rightarrow 50^\circ}$	$10^6\,\alpha^\circ_{12\rightarrow 48^\circ}$
Results obtained with glass vessels.		
Air, CO_2-free	3672	—
Ethylene	3736	—
Nitrous oxide	3731	—
Carbon dioxide	3726	3728
Results with glass vessels corrected for adsorption.		
Ethylene	3735	—
Nitrous oxide	3729	—
Carbon dioxide	3723	—
Results obtained with silica vessel.		
Carbon dioxide	—	3725
Dimethyl ether	—	3920
Nitric oxide	—	3679
Carbon monoxide	—	3674
Sulphur hexafluoride	—	3808

Summary.

By the use of a Callendar constant pressure air thermometer determinations have been made of the volume coefficients of expansion of ethylene, carbon dioxide, nitrous oxide, nitric oxide, carbon monoxide, dimethyl ether, and sulphur hexafluoride, at several pressures between the temperature limits of 25°–50° C. in Series I, and 11°–48° in Series II.

Measurements were made using two expansion bulbs, one of glass and the other of fused silica. Those for carbon dioxide, nitrous oxide and ethylene obtained in the glass vessel when extrapolated gave values for the coefficient at zero pressure markedly greater than the accepted value, but those carried out in silica yielded results in close agreement with this constant. This discrepancy is shown to be due to the greater adsorption on glass than on silica surfaces and when easily condensable gases are used gives rise to appreciable errors.

Results of Calculations of Atomic Wave Functions. II.—*Results for* K^+ *and* Cs^+.

By D. R. Hartree, F.R.S.

(Received October 21, 1933.)

§ 1. *Introduction.*

In a recent paper[*] I presented the results of calculations of approximate wave functions of two atoms, based on the method of the "self-consistent field",[†] these calculations having been carried out to a fairly high degree of numerical accuracy (for work of this kind) as regards both precision of the work and the approximation to the self-consistent field attained, in order that the results published should be quite dependable. I also gave a survey of the situation which led to such calculations being undertaken, and mentioned other atoms for which they were being made.

This paper presents a second instalment of such results, namely, those for the atoms K^+ and Cs^+. Of these atoms, Cs is the heaviest for which calculations of the self-consistent field have so far been completed, though work on a still heavier atom, namely, mercury, has been started, and it is hoped that rough results, at least, will be available before long.

Other atoms for which it is intended to obtain results of the numerical accuracy of those in this paper are Al^{+3}, Rb^+ (as already stated in I) and also F^-, Al^+, Ca^{+2}, Ag^+.

Since the previous paper, I, was prepared, it has been suggested[‡] that, in addition to the information there tabulated, it would be desirable to give for the positive ions the total $2Z_p$ for the complete atom (Z_p/r being the potential at radius r) as this is a quantity required in calculating wave functions of the series electron. This information is given for the two atoms for which the results are given here, and also for Cu^+ for which the other results were given in I. The value of $2v_0 = \left[\frac{d}{dr}(2Z_p)\right]_{r=0}$ is also given as it also may be required, v_0 is the potential at the origin of the Schrödinger distribution of the electrons of the ion.

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[*] Hartree, 'Proc. Roy. Soc.,' A, vol. 141, p. 282 (1933). This paper will be referred to as I.

[†] Hartree, 'Proc. Camb. Phil. Soc.,' vol. 24, pp. 89, 111 (1928).

[‡] I am indebted to Mr. J. McDougall for the suggestion.

In using the "self-consistent field" approximation for the many-electron atom to calculate wave functions of an atom with a series electron, we should strictly calculate the self-consistent field of the whole system (core + series electron). The perturbation of the wave functions of the core by the series electron is usually neglected; that is to say, the wave functions of the series electron are calculated as wave functions in a field of potential Z_p/r, where Z_p is constructed from the wave functions for the self-consistent field of the ion. This is probably a good approximation for alkali and alkali-like atoms and ions, for which the core is inert-gas-like and is not sensitive to perturbing influences, but it is doubtful if it is a good approximation for atoms of the Cu, Ag, Au group and ions of similar structure, on account of the sensitiveness of the $(3d)^{10}$ group of core-electrons, already mentioned in the previous paper. However, a table of $2Z_p$ for the Cu^+ ion is also given here, as the first stage, at any rate, in calculating series electron wave functions will be to neglect the perturbation of the core by the series electron, and the effects of this perturbation can then be added by means of a variation calculation.

§ 2. *Results for* K^+.

On account of an error in the previous calculations from which the contributions to Z for the "standard calculations" (*cf.* I, p. 283) were estimated, the difference between the estimated and the calculated Z for these calculations was as great as 0·10 for the $(3p)^6$ group. Two further sets of revised estimates were made, and the difference between estimated and calculated Z is nowhere greater than 0·005 in the contribution from any group, or greater than 0·01 in the aggregate.

Table I.—K^+ Wave Functions.

Table of P/r^{l+1} for small r.

r.	$(1s)$.	$(2s)$.	$(2p)$.	$(3s)$.	$(3p)$.
0·000	100·00	100·00	500·0	100·00	500·0
0·005	90·94	90·86	476·9	90·85	476·9
0·010	82·72	82·41	455·0	82·39	455·0
0·015	75·25	74·59	434·3	74·55	434·2
0·020	68·47	67·37	414·7	67·29	414·4

The results are given in Tables I and II.

Table of P.

r.	(1*s*).	(2*s*).	(2*p*).	(3*s*).	(3*p*).
0·005	0·455	0·454	0·012	0·454	0·012
0·010	0·827	0·824	0·045	0·824	0·045
0·015	1·129	1·119	0·098	1·118	0·098
0·020	1·369	1·347	0·166	1·346	0·166
0·03	1·701	1·635	0·341	1·630	0·340
0·04	1·880	1·741	0·554	1·730	0·552
0·05	1·949	1·708	0·791	1·688	0·788
0·06	1·940	1·569	1·043	1·539	1·037
0·07	1·879	1·353	1·302	1·311	1·292
0·08	1·783	1·081	1·561	1·027	1·544
0·09	1·666	0·773	1·814	0·706	1·789
0·10	1·539	0·442	2·059	+0·363	2·022
0·12	1·277	−0·245	2·510	−0·344	2·442
0·14	1·031	−0·916	2·899	−1·024	2·788
0·16	0·817	−1·531	3·221	−1·634	3·052
0·18	0·637	−2·070	3·475	−2·150	3·234
0·20	0·492	−2·525	3·666	−2·562	3·337
0·22	0·376	−2·895	3·797	−2·867	3·366
0·24	0·286	−3·184	3·876	−3·069	3·327
0·26	0·215	−3·397	3·909	−3·174	3·228
0·28	0·162	−3·543	3·903	−3·191	3·076
0·30	0·121	−3·631	3·864	−3·129	2·878
0·35	0·058	−3·645	3·658	−2·693	2·227
0·40	0·027	−3·457	3·353	−1·968	1·422
0·45	0·013	−3·154	3·001	−1·074	0·536
0·50	0·005	−2·797	2·638	−0·103	−0·377
0·55	0·003	−2·429	2·286	+0·875	−1·276
0·60	0·001	−2·074	1·957	1·812	−2·131
0·7		−1·457	1·395	3·446	−3·641
0·8		−0·986	0·968	4·673	−4·827
0·9		−0·650	0·657	5·486	−5·684
1·0		−0·421	0·440	5·937	−6·245
1·1		−0·268	0·291	6·096	−6·557
1·2		−0·169	0·190	6·037	−6·671
1·4		−0·066	0·080	5·511	−6·490
1·6		−0·025	0·033	4·733	−5·988
1·8		−0·009	0·014	3·914	−5·348
2·0		−0·003	0·005$_5$	3·156	−4·674
2·2		−0·001	0·002	2·501	−4·023
2·4			0·001	1·955	−3·423
2·6				1·513	−2·887
2·8				1·162	−2·417
3·0				0·886	−2·012
3·2				0·673	−1·665
3·4				0·508	−1·372
3·6				0·382	−1·126
3·8				0·286	−0·920
4·0				0·213	−0·750

Table I.—(continued).

r.	(1s).	(2s).	(2p).	(3s).	(3p).
4·5				0·101	−0·444
5·0				0·047	−0·259
5·5				0·022	−0·149
6·0				0·010	−0·085
6·5				0·004$_5$	−0·048
7·0				0·002	−0·027
8				0·000$_5$	−0·008
9					−0·0025
10					−0·001

	1s.	2s.	2p.	3s.	3p.
ϵ	267·35	26·68	21·97	3·084	1·864
$\int_0^\infty P^2\,dr$	0·3816	4·902	5·820	40·27	61·37

Table II.—K$^+$, contributions to Z, and total Z_p.

Contributions to Z.						Total $2Z_p$.
r.	$(1s)^2$.	$(2s)^2$.	$(2p)^6$.	$(3s)^2$.	$(3p)^6$.	($2v_0 = -147\cdot8$).
0·000	2·000	2·000	6·000	2·000	6·000	38·000
0·005	1·998	2·000	6·000	2·000	6·000	37·264
0·010	1·987	1·999	6·000	2·000	6·000	36·539
0·015	1·963	1·997	6·000	2·000	6·000	35·833
0·020	1·921	1·994	6·000	1·999	6·000	35·151
0·03	1·795	1·985	5·999	1·998	6·000	33·867
0·04	1·625	1·973	5·997	1·997	6·000	32·691
0·05	1·431	1·961	5·992	1·995	5·999	31·617
0·06	1·232	1·950	5·983	1·994	5·998	30·631
0·07	1·040	1·941	5·969	1·993	5·997	29·718
0·08	0·864	1·935	5·947	1·992	5·995	28·866
0·10	0·573	1·930	5·879	1·991	5·989	27·304
0·12	0·365	1·929	5·771	1·991	5·979	25·882
0·14	0·225	1·926	5·619	1·990	5·966	24·567
0·16	0·136	1·913	5·426	1·989	5·950	23·340
0·18	0·080	1·886	5·193	1·986	5·929	22·194
0·20	0·047	1·843	4·929	1·980	5·908	21·127
0·22	0·028	1·783	4·642	1·973	5·886	20·136
0·24	0·016	1·707	4·337	1·964	5·864	19·219
0·26	0·009	1·618	4·025	1·954	5·843	18·375
0·28	0·005	1·520	3·710	1·944	5·824	17·599
0·30	0·003	1·415	3·399	1·934	5·806	16·887

Table II—(continued).

	Contributions to Z.					Total $2Z_p$.
r.	$(1s)^2$.	$(2s)^2$.	$(2p)^6$.	$(3s)^2$.	$(3p)^6$.	
0·35	0·001	1·142	2·665	1·912	5·774	15·353
0·40		0·882	2·029	1·899	5·757	14·107
0·45		0·659	1·509	1·893	5·752	13·073
0·50		0·477	1·098	1·892	5·752	12·189
0·55		0·337	0·785	1·891	5·748	11·411
0·60		0·234	0·553	1·886	5·734	10·706
0·7		0·107	0·265	1·850	5·649	9·444
0·8		0·047	0·122	1·766	5·470	8·323
0·9		0·020	0·055	1·636	5·197	7·321
1·0		0·009	0·024	1·473	4·846	6·435
1·1		0·004	0·011	1·292	4·443	5·666
1·2		0·002	0·005	1·108	4·014	5·009
1·4			0·001	0·772	3·158	3·994
1·6				0·512	2·392	3·300
1·8				0·324	1·761	2·839
2·0				0·201	1·270	2·539
2·2				0·122	0·901	2·344
2·4				0·072	0·630	2·217
2·6				0·043	0·435	2·137
2·8				0·025	0·298	2·087
3·0				0·014	0·202	2·055
3·2				0·008	0·137	2·035
3·4				0·005	0·092	2·022
3·6				0·003	0·061	2·014
3·8				0·002	0·041	2·009
4·0				0·001	0·027	$2{\cdot}005_8$
4·5					0·010	$2{\cdot}001_9$
5·0					0·003	$2{\cdot}000_5$
5·5					0·001	$2{\cdot}000_1$

§ 3. *Results for* Cs^+.

The maximum difference between estimated and calculated total Z, for the standard calculations, was 0·05. Revised estimates for the contribution from the $(3p)^6$ group only, for which the differences were largest, were first made and the variations from the standard calculations found; then a set of revised estimates for the whole atom was made, giving the results here tabulated for which the maximum difference between the estimated and calculated contributions to Z from any one group is 0·013 for the $(4d)^{10}$, which is the most sensitive and the most difficult to estimate; the maximum for any other group is 0·005, and the maximum difference for the total Z is 0·02. For an atom containing as many electron groups (eleven) as this, random values of the difference between estimated and calculated contributions may add up to an appreciable aggregate, if they all happen to be of one sign, even if each single contribution is estimated correctly to the nearest 0·01, and this has occurred in some instances for this atom.

The results are given in Tables III, IV, and V. In Table III, unnormalized wave functions P are tabulated, for the reasons given in the earlier paper (I). They are usually tabulated with the arbitrary constant of integration chosen so that (P/r^{l+1}) at $r = 0$ is the same for different wave functions with the same l; but for (1*s*) and (2*p*) they are tabulated with the value of (P/r^{l+1}) at $r = 0$ twice as big as for the other *s* and *p* wave functions respectively, in order to obtain adequate numerical accuracy without including an extra decimal place in the tabulated functions.

In order to avoid unnecessary extension of Table IV, the contributions from different electron groups are tabulated at different intervals for small r, as the contribution from the outer groups vary so slowly in this region. This makes it inconvenient to include $2Z_p$ for the complete ion in the same table, as is done in Table II for K^+, so this quantity is tabulated separately in Table V.

The observed values of ν/R for the X-ray terms* are given for comparison with the values of the energy parameters ε for the various central field problems. The correspondence is not on the whole so close as for Cu^+, for which similar results were given in I, but this is mainly because in obtaining the value of ε no account has been taken of spin and relativity effects. An attempt to obtain rough estimates of the contributions to ν/R from spin and from the relativistic variation of mass with velocity has been made by multiplying the calculated contributions for each (nl) term for Rb^+† by the ratio of the observed (np) spin doublet separations for Rb^+ and Cs^+; for $n = 4$ the Rb^+ spin separation has not been observed, and the calculated value has been taken instead.

Values of ν/R, less estimated spin and relativity contributions estimated in this way, are also given, and it will be seen that their agreement with the energy parameters ε is strikingly close; the difference is greatest for the *s* terms, for which the method of estimating the spin and relativity effects is least reliable.

§ 4. *Further Results for* Cu^+.

In Table VI, $2Z_p$ for the Cu^+ ion is tabulated. In using it for the calculation of wave functions of the series electron, it must be remembered that for this

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* Taken from Siegbahn's, 'Spectroskopie der Rontgenstrahlen' (1931).

† See Hartree, 'Proc. Camb. Phil. Soc.,' *loc. cit.*, p. 124.

Table III.—Cs^+. Radial Wave Functions.

Table of P/r^{l+1}.

r.	(1s).	(2s).	(2p).	(3s).	(3p).	(3d).	(4s)	(4p).	(4d).	(5s).	(5p).
0·000	400·0	200·0	4000	200·0	2000	10000	200·0	2000	10000	200·0	2000
0·002	358·3	178·9	3786	178·9	1893	9640	178·9	1893	9640	178·9	1893
0·004	321·0	159·6	3585	159·4	1792	9300	159·4	1791	9300	159·4	1791
0·006	287·7	141·8	3395	141·5	1696	8970	141·5	1695	8970	141·5	1695
0·008	257·8	125·6	3215	125·1	1605	8650	125·0	1604	8650	125·0	1604
0·010	231·2	110·7	3046	110·0	1519	8350	109·9	1517	8340	109·9	1517
0·015	175·7	78·8	2662	77·5	1322	7640	77·3	1320	7630	77·2	1320
0·020	133·7	53·3	2329	51·5	1150	7000	51·2	1147	6990	51·1	1146

Table of P.

r.	(1s).	(2s).	(2p).	(3s).	(3p).	(3d).	(4s).	(4p).	(4d).	(5s).	(5p).
0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·002	0·717	0·358	0·015	0·358	0·008	0·000	0·358	0·008	0·000	0·358	0·008
0·004	1·284	0·638	0·057	0·638	0·029	0·001	0·638	0·029	0·001	0·638	0·029
0·006	1·726	0·851	0·122	0·849	0·061	0·002	0·849	0·061	0·002	0·849	0·061
0·008	2·062	1·005	0·206	1·001	0·103	0·004	1·000	0·103	0·004	1·000	0·103
0·010	2·312	1·107	0·305	1·100	0·152	0·008	1·099	0·152	0·008	1·099	0·152
0·015	2·635	1·182	0·599	1·163	0·297	0·026	1·159	0·297	0·026	1·159	0·297
0·020	2·673	1·066	0·932	1·030	0·460	0·056	1·023	0·459	0·056	1·022	0·459
0·025	2·544	0·828	1·274	0·771	0·624	0·100	0·760	0·622	0·100	0·758	0·621
0·030	2·324	0·516	1·608	0·438	0·780	0·159	0·422	0·775	0·159	0·420	0·774
0·035	2·066	0·168	1·919	0·070	0·919	0·232	0·051	0·911	0·231	0·048	0·910
0·040	1·799	−0·191	2·199	−0·303	1·037	0·318	−0·324	1·025	0·317	−0·328	1·023
0·045	1·543	−0·541	2·443	−0·660	1·131	0·417	−0·682	1·113	0·414	−0·685	1·111
0·050	1·307	−0·870	2·649	−0·986	1·199	0·527	−1·006	1·175	0·522	−1·010	1·172
0·06	0·913	−1·435	2·948	−1·511	1·259	0·773	−1·522	1·220	0·763	−1·524	1·214
0·07	0·620	−1·859	3·107	−1·842	1·224	1·045	−1·834	1·166	1·026	−1·832	1·157
0·08	0·414	−2·141	3·148	−1·980	1·109	1·332	−1·941	1·029	1·299	−1·934	1·017
0·09	0·272	−2·299	3·097	−1·944	0·929	1·623	−1·867	0·827	1·571	−1·853	0·811
0·10	0·177	−2·354	2·976	−1·764	0·703	1·909	−1·643	0·579	1·832	−1·621	0·560
0·11	0·114	−2·329	2·809	−1·472	0·445	2·184	−1·305	0·301	2·074	−1·275	0·280
0·12	0·073	−2·246	2·610	−1·099	0·169	2·441	−0·887	0·010	2·290	−0·846	−0·013
0·14	0·029	−1·972	2·176	−0·218	−0·391	2·888	+0·066	−0·563	2·631	+0·114	−0·587
0·16	0·012	−1·639	1·749	+0·700	−0·910	3·232	1·013	−1·064	2·834	1·064	−1·084
0·18	0·005	−1·312	1·368	1·541	−1·350	3·471	1·824	−1·450	2·896	1·865	−1·460
0·20	0·002	−1·021	1·048	2·244	−1·696	3·609	2·426	−1·703	2·826	2·445	−1·698
0·22	0·001	−0·777	0·790	2·784	−1·946	3·661	2·793	−1·822	2·640	2·778	−1·796
0·24		−0·582	0·588	3·162	−2·106	3·640	2·929	−1·817	2·355	2·868	−1·766
0·26		−0·431	0·432	3·391	−2·189	3·560	2·856	−1·706	1·992	2·742	−1·627
0·28		−0·315	0·316	3·493	−2·207	3·434	2·607	−1·507	1·568	2·434	−1·398
0·30		−0·228	0·229	3·493	−2·175	3·276	2·216	−1·239	1·102	1·983	−1·101
0·32		−0·164	0·165	3·412	−2·103	3·095	1·719	−0·921	0·608	1·428	−0·756
0·34		−0·117	0·118	3·271	−2·003	2·899	1·149	−0·571	0·101	0·807	−0·382
0·36		−0·083	0·084	3·089	−1·884	2·696	0·536	−0·202	−0·408	0·151	+0·007
0·38		−0·059	0·060	2·880	−1·753	2·491	−0·096	+0·174	−0·910	−0·511	0·395
0·40		−0·042	0·042	2·657	−1·617	2·289	−0·725	+0·544	−1·397	−1·156	0·772

Table III—(continued).

r.	(1*s*).	(2*s*).	(2*p*).	(3*s*).	(3*p*).	(3*d*).	(4*s*).	(4*p*).	(4*d*).	(5*s*).	(5*p*).
0·45		−0·017	0·018	2·090	−1·277	1·814	−2·187	1·403	−2·509	−2·580	1·610
0·50		−0·007	0·007	1·578	−0·974	1·402	−3·374	2·107	−3·430	−3·606	2·235
0·55		−0·003	0·003	1·155	−0·722	1·064	−4·228	2·631	−4·138	−4·175	2·617
0·60		−0·001	0·001	0·826	−0·525	0·794	−4·758	2·968	−4·641	−4·306	2·763
0·65				0·581	−0·375	0·587	−5·009	3·151	−4·961	−4·061	2·702
0·70				0·402	−0·265	0·429	−5·037	3·206	−5·126	−3·519	2·470
0·75				0·275	−0·185	0·311	−4·901	3·161	−5·165	−2·760	2·107
0·80				0·187	−0·128	0·224	−4·651	3·045	−5·107	−1·855	1·648
0·9				0·084	−0·060	0·114	−3·966	2·685	−4·789	+0·156	0·566
1·0				0·037	−0·028	0·058	−3·215	2·256	−4·317	2·159	−0·589
1·1				0·016	−0·013	0·029	−2·516	1·834	−3·787	3·949	−1·694
1·2				0·007	−0·006	0·015	−1·919	1·456	−3·255	5·426	−2·683
1·3				0·003	−0·003	0·007$_5$	−1·436	1·134	−2·756	6·560	−3·521
1·4				0·001$_5$	−0·001$_5$	0·004	−1·059	0·872	−2·305	7·364	−4·199
1·5				0·000$_5$	−0·000$_5$	0·002	−0·771	0·662	−1·910	7·869	−4·721
1·6						0·001	−0·556	0·498	−1·571	8·121	−5·099
1·8							−0·283	0·277	−1·044	8·049	−5·496
2·0							−0·141	0·151	−0·683	7·484	−5·531
2·2							−0·069	0·081	−0·442	6·674	−5·330
2·4							−0·034	0·043	−0·284	5·784	−4·988
2·6							−0·016	0·023	−0·181	4·912	−4·572
2·8							−0·007$_5$	0·012	−0·115	4·108	−4·128
3·0							−0·003$_5$	0·006	−0·073	3·396	−3·684
3·2							−0·002	0·003	−0·046	2·781	−3·256
3·4							−0·001	0·001$_5$	−0·029	2·261	−2·857
3·6								0·001	−0·018	1·827	−2·492
3·8									−0·011	1·469	−2·161
4·0									−0·007	1·176	−1·865
4·5									−0·002	0·663	−1·269
5·0										0·367	−0·847
5·5										0·200	−0·556
6·0										0·108	−0·360
6·5										0·058	−0·231
7·0										0·030	−0·146
8										0·008	−0·058
9										0·002	−0·022
10										0·000$_5$	−0·008
11											−0·003
12											−0·001

	ε.	ν/R.	(ν/R) — (estimated spin and relativity contributions).	$\int_0^\infty P^2\,dr$.
(1*s*)	2543·1	2649·8	2574	0·2448$_1$
(2*s*)	385·45	420·3	389	0·5859
(2*p*)	365·33	394·8 369·3	363	1·0419
(3*s*)	79·72	89·5	82	2·985$_5$
(3*p*)	70·42	77·8 72·9	71	1·2293
(3*d*)	53·42	54·6 53·6	54	3·5478

	ε.	ν/R.	(ν/R) — (estimated spin and relativity contributions).	$\int_0^\infty P^2\,dr$.
4*s*	15·096	17·0	15·6	13·45$_5$
4*p*	11·702	12·1 11·1	10·8	5·899
4*d*	5·922	5·8 5·7	5·7	19·043
5*s*	2·180$_5$	1·9	1·9	91·62
5*p*	1·341	(0·2)	(0·2)	54·56

Table IV.—Cs$^+$. Contributions to Z.

Table of $2\,(2l+1)\,[1 - Z_0\,(nl, nl/r)]$.

r.	$(1s)^2$.	$(2s)^2$.	$(2p)^6$.
0·000	2·000	2·000	6·000
0·001	2·000	2·000	6·000
0·002	1·997	2·000	6·000
0·003	1·991	1·999	6·000
0·004	1·980	1·998	6·000
0·005	1·964	1·996	6·000
0·006	1·942	1·994	6·000
0·008	1·883	1·988	5·999
0·010	1·804	1·980	5·999
0·015	1·548	1·958	5·993
0·020	1·256	1·935	5·976
0·025	0·976	1·920	5·940
0·030	0·733	1·912	5·880
0·035	0·535	1·910	5·790
0·040	0·383	1·909	5·668
0·045	0·269	1·907	5·512
0·050	0·186	1·898	5·325
0·06	0·086	1·851	4·869
0·07	0·038	1·757	4·338
0·08	0·016	1·618	3·772
0·09	0·007	1·449	3·208
0·10	0·003	1·263	2·675
0·11	0·001	1·074	2·192
0·12		0·895	1·768
0·13		0·732	1·407
0·14		0·589	1·106
0·16		0·365	0·662
0·18		0·216	0·383
0·20		0·123	0·215

r.	$(3s)^2$.	$(3p)^6$.	$(3d)^{10}$.	$(4s)^2$.	$(4p)^6$.	$(4d)^{10}$.
0·000	2·000	6·000	10·000	2·000	6·000	10·000
0·005	1·999	6·000	10·000	2·000	6·000	10·000
0·010	1·996	6·000	10·000	2·000	6·000	10·000
0·015	1·992	5·999	10·000	1·999	6·000	10·000
0·020	1·988	5·995	10·000	1·998	5·999	10·000
0·03	1·984	5·977	10·000	1·996	5·995	10·000
0·04	1·983	5·936	9·998	1·996	5·986	9·999
0·05	1·980	5·874	9·993	1·995	5·974	9·998
0·06	1·969	5·799	9·981	1·993	5·959	9·996
0·07	1·950	5·723	9·958	1·989	5·944	9·992
0·08	1·925	5·656	9·918	1·984	5·932	9·985
0·09	1·899	5·605	9·856	1·979	5·923	9·975
0·10	1·876	5·571	9·768	1·974	5·918	9·958
0·11	1·858	5·555	9·650	1·970	5·915	9·938
0·12	1·847	5·549	9·499	1·968	5·915	9·913
0·14	1·840	5·546	9·095	1·968	5·913	9·849
0·16	1·839	5·501	8·563	1·967	5·899	9·770
0·18	1·821	5·374	7·926	1·960	5·866	9·682
0·20	1·772	5·144	7·217	1·946	5·815	9·596
0·22	1·686	4·817	6·469	1·926	5·751	9·517
0·24	1·566	4·414	5·716	1·902	5·682	9·450
0·26	1·421	3·961	4·983	1·877	5·619	9·400
0·28	1·262	3·487	4·293	1·854	5·566	9·367
0·30	1·097	3·017	3·657	1·837	5·527	9·347
0·32	0·937	2·569	3·084	1·825	5·503	9·340
0·34	0·786	2·157	2·577	1·819	5·492	9·338
0·36	0·651	1·788	2·135	1·817	5·488	9·338
0·38	0·532	1·464	1·756	1·817	5·488	9·333
0·40	0·429	1·187	1·434	1·816	5·485	9·319

r.	$(5s)^2$.	$(5p)^6$.
0·00	2·000	6·000
0·04	2·000	5·999
0·08	1·998	5·993
0·12	1·996	5·991
0·16	1·995	5·989
0·20	1·992	5·979
0·24	1·986	5·966
0·28	1·979	5·954
0·32	1·976	5·949
0·36	1·975	5·948
0·40	1·974	5·947
0·45	1·970	5·939
0·50	1·959	5·918
0·55	1·942	5·885
0·60	1·922	5·845
0·65	1·903	5·803
0·70	1·887	5·767
0·75	1·876	5·738
0·80	1·870	5·718
0·9	1·867	5·703
1·0	1·863	5·701
1·1	1·842	5·686
1·2	1·793	5·631
1·3	1·715	5·523
1·4	1·608	5·359
1·5	1·480	5·139
1·6	1·340	4·372
1·8	1·051	4·246
2·0	0·784	3·572

0·22		0·068	0·118
0·24		0·037	0·064
0·26		0·019	0·034
0·28		0·010	0·017
0·30		0·005	0·009
0·32		0·002	0·005
0·34		0·001	0·002
0·36			0·001
0·38			
0·40			

0·45	0·239	0·675	0·841	1·798	5·432	9·215
0·50	0·126	0·366	0·477	1·739	5·271	8·980
0·55	0·064	0·191	0·263	1·630	4·981	8·599
0·60	0·031	0·096	0·141	1·478	4·578	8·089
0·65	0·015	0·047	0·075	1·299	4·099	7·479
0·70	0·007	0·023	0·039	1·111	3·582	6·808
0·75	0·003	0·011	0·020	0·926	3·064	6·112
0·80	0·001	0·005	0·010	0·756	2·573	5·418
0·9		0·001	0·002	0·478	1·731	4·123
1·0				0·285	1·109	3·029
1·1				0·163	0·683	2·165
1·2				0·090	0·408	1·513
1·3				0·049	0·238	1·039
1·4				0·026	0·137	0·702
1·5				0·014	0·077	0·469
1·6				0·007	0·042	0·310
1·8				0·002	0·013	0·132
2·0					0·004	0·055
2·2					0·001	0·022
2·4						0·009
2·6						0·003
2·8						0·001

2·2	0·564	2·920
2·4	0·395	2·332
2·6	0·270	1·829
2·8	0·181	1·412
3·0	0·120	1·076
3·2	0·078	0·811
3·4	0·050	0·606
3·6	0·032	0·449
3·8	0·020	0·330
4·0	0·013	0·241
4·5	0·004	0·106
5·0	0·001	0·049
5·5		0·019
6·0		0·007
6·5		0·003
7·0		0·001

Table V.—Cs^+. $2Z_p$ for complete ion.

r.	$2Z_p$.	r.	$2Z_p$.	r.	$2Z_p$.	r.	$2Z_p$.
0·000	110·00	0·14	61·775	0·9	12·983	4·5	$2{\cdot}022_6$
0·002	108·71	0·16	57·955	1·0	11·329	5·0	$2{\cdot}008_5$
0·004	107·44	0·18	54·47	1·1	10·013	5·5	$2{\cdot}003_1$
0·006	106·20	0·20	51·295	1·2	8·927	6·0	$2{\cdot}001_1$
0·008	105·00	0·22	48·405	1·3	8·002	6·5	$2{\cdot}000_4$
0·010	103·83	0·24	45·79	1·4	7·202	7·0	$2{\cdot}000_1$
		0·26	43·435	1·5	6·502		
0·015	101·09	0·28	41·31	1·6	5·885		
0·020	98·56	0·30	39·385			$2v_0 = -646$	
0·025	96·21			1·8	4·866		
0·030	93·995	0·32	37·64	2·0	4·088		
0·035	91·885	0·34	36·03	2·2	3·504		
0·040	89·865	0·36	34·55	2·4	3·073		
		0·38	33·17	2·6	2·759		
0·05	86·05	0·40	31·865	2·8	2·533		
0·06	82·505			3·0	2·373		
0·07	79·215	0·45	28·885				
0·08	76·17	0·50	26·210	3·2	2·259		
0·09	73·35	0·55	23·786	3·4	2·179		
0·10	70·73	0·60	21·604	3·6	2·124		
0·11	68·285	0·65	19·659	3·8	2·084		
0·12	65·99	0·70	17·942	4·0	$2{\cdot}057_6$		
		0·75	16·438				
		0·80	15·126				

Table VI.—Cu^+. $2Z_p$ for complete ion.

r.	$2Z_p$.	r.	$2Z_p$.	r.	$2Z_p$.	r.	$2Z_p$.
0·000	58·00	0·18	31·573	1·1	4·858	4·5	$2{\cdot}004_0$
0·005	56·67	0·20	29·960	1·2	4·286	5·0	$2{\cdot}001_3$
0·010	55·38	0·22	28·497	1·3	3·843	5·5	$2{\cdot}000_4$
0·015	54·145	0·24	27·160	1·4	3·496	6·0	$2{\cdot}000_1$
0·020	52·98	0·26	25·925			>6	$2{\cdot}000_0$
0·025	51·875	0·28	24·774	1·6	3·003		
0·030	50·835	0·30	23·692	1·8	2·682		
0·035	49·85			2·0	2·469		
0·040	48·915	0·35	21·217	2·2	2·324	$2v_0 = -269$	
		0·40	18·995	2·4	2·224		
0·05	47·17	0·45	16·980	2·6	2·155		
0·06	45·56	0·50	15·161	2·8	2·107		
0·07	44·05	0·55	13·534	3·0	2·074		
0·08	42·62	0·60	12·093				
0·09	41·26			3·2	2·051		
0·10	39·96	0·7	9·724	3·4	2·035		
		0·8	7·939	3·6	2·024		
0·12	37·539	0·9	6·606	3·8	$2{\cdot}016_4$		
0·14	35·343	1·0	5·609	4·0	$2{\cdot}011_1$		
0·16	33·360						

atom the perturbation of the core wave functions by the series electron may be appreciable, as pointed out at the end of § 1.

§ 5. *Summary.*

In continuation of the plan outlined in a previous paper for making generally available the results of calculations of atomic wave functions by the method of the "self-consistent field," results for K^+ and Cs^+ are here presented, also some additional results for Cu^+.

As mentioned in the previous paper, the "standard calculations" on which the results are based were carried out professionally, and I wish to acknowledge my thanks to the Government Grant Committee for a grant which enabled me to have the benefit of such assistance.

The Effect of Accommodation on Heat Conduction through Gases.

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(Communicated by G. P. Thomson, F.R.S.—Received August 14, 1933.)

Introduction.

An experimental determination of the thermal conductivity of a gas necessarily involves a number of corrections which must either be determined or eliminated before an absolute value can be obtained. With the "hot-wire" method the inherent errors are: (1) the heat lost by radiation; (2) the heat losses due to convection; (3) the temperature discontinuity between the gas and solid surfaces; and (4) the fact that the interchange of energy between the gas molecules and the solid surfaces is not perfect. The true temperature attained by a molecule striking a hot surface always being less than the temperature of that surface.

Previous investigators using this method have applied a correction for the heat lost by radiation, determined by measuring the heat loss in the best obtainable vacuum; while the convective heat loss has been eliminated, either by simply reducing the pressure or by using a double system of tubes. Both methods are debatable, for the first is very inaccurate, while the second necessarily complicates the experimental arrangement.

The third and fourth corrections, though usually small and depending very largely on the dimensions of the apparatus and the nature of the gas, have in general been neglected; such a correction may, however, be of considerable importance in an accurate determination of the thermal conductivity of a gas. In view of the fact that the temperature discontinuity depends on the pressure of the gas, the thermal conductivity may be deduced from observations of the heat transfer at different pressures, as described in the present paper.

The "hot-wire" method, developed by Gregory and Archer,* has recently been modified by Gregory in relation to the effect of temperature on the thermal conductivity of hydrogen. The successful issue of the experiments has suggested an extension of the method to an investigation on the heavier gases in which convection is more marked; on this account the temperature drop relation is restricted to a range of pressures much smaller than for hydrogen.

The present paper deals with the modifications necessary in the measurement of the thermal conductivity of gases of higher molecular weight and a determination of their accommodation coefficients.

Theory of the Method.

In the "hot-wire" method of measurement, a wire which is heated electrically is disposed along the axis of a cylindrical glass tube containing the gas, the external temperature of the tube being maintained at a constant temperature. The temperature of the wire is determined by measuring its resistance; it may be shown that the temperature is only uniform along the centre portion of the wire owing to conduction of heat along the lead wires, which are at the temperature of the surrounding thermostat. Hence to compensate for the end-effects, a similar but shorter tube is placed in gaseous connection with the main tube, and the two wires inserted in the main and compensating arms of a Callendar and Griffith's Bridge.

Under these conditions the observations correspond to the emission of heat from a length of wire, l, given by the difference in length of the wires in the two tubes. The temperature of this length of wire can be accurately maintained at a uniform temperature θ_1, by varying the current through the wires, while the temperature can be determined from the measurement of the effective resistance, *i.e.*, the difference in resistances of the two wires.

In such a system the heat conduction W through the gas is given by the equation

$$W = \frac{2\pi K\, l(\theta_1 - \theta_2)}{\log_e \frac{r_2}{r_1}}, \tag{1}$$

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* 'Proc. Roy. Soc.,' A, vol. 110, p. 91 (1926).

where r_1 is the radius of the wire, r_2 and θ_2 the radius and temperature of the inner surface of the glass tube, K being the thermal conductivity of the gas at a mean temperature of the wire and inner surface of the tube.

If C is the current flowing through the wires, R the effective resistance, and J the mechanical equivalent of heat. Then

$$W = \frac{C^2R}{J} - \phi - \psi,$$

where ϕ and ψ are the heat losses due to radiation and convection respectively.

The corrections for the heat loss due to radiation, given in Table I, were calculated from the results of Gregory and Archer (*loc. cit.*), who, using a double system of tubes, measured the heat loss from bright platinum at different temperatures in the best obtainable vacuum. The conductivity of the residual gas could be eliminated by reason of the different dimensions of the two systems.

Table I.

T ° C.	ϕ Cals.	T ° C.	ϕ Cals.
24·1	0·000124	8·4	0·000022
19·5	0·000094	6·5	0·000018
14·9	0·000064	4·7	0·000012

In Table I, T is the temperature difference across the gas and ϕ the heat radiated from the length of wire l used in the present experiment. This correction never amounted to more than 0·5% of the total heat transfer.

The corrections due to convection and temperature discontinuity will now be considered. With regard to the former, no rigorous theoretical treatment has yet been attempted, though it is generally accepted that such losses may be greatly reduced by a careful consideration of the dimensions and design of the apparatus. For the temperature drop, however, the researches of Knudsen and Smoluchowski have placed it on a firm theoretical basis.

A consideration of the analogous " slip " effect in the viscosity of gases led Kundt and Warburg* to predict a temperature discontinuity for heat conduction through gases and to define it as proportional to the temperature gradient along the normal to the surface, *i.e.*,

$$\Delta\theta = -\gamma \frac{d\theta}{dn},$$

where γ is the coefficient of discontinuity.

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* 'Pogg. Ann.,' vol. 156, p. 177 (1875).

Now, according to Knudsen,* when a gas molecule strikes a hot surface the interchange of energy between the molecules and the solid surface is not perfect. Hence molecules at a temperature θ striking a hot surface of temperature θ_1 will leave that surface with a temperature θ', which is less than that of the surface and related to θ_1 by

$$\theta' - \theta = a\,(\theta_1 - \theta).$$

"a" being known as the accommodation coefficient of the gas with respect to the surface under consideration.

Assuming Maxwell's hypothesis that molecules are centres of force repelling one another according to the inverse fifth law of distance, it has been shown by Smoluchowski† that

$$\gamma = \frac{15}{2\pi}\,\lambda\,\frac{2-a}{2a},$$

λ being the mean free path.

Applying the above considerations to the cylindrical distribution of temperature operative in the present experiment, the modified Fourier equation is

$$W = \frac{2\pi Kl\,(\theta_1 - \theta_2)}{\log_e \frac{r_2}{r_1} + \frac{\gamma}{r_1} + \frac{\gamma'}{r_2}}, \qquad (2)$$

where the coefficients γ and γ' refer to the wire and wall respectively.

It is evident from the above equation that the temperature drop is inversely proportional to the radius of the enclosing surface; the radius of the wall being about 100 times that of the wire in the present experiment, the temperature discontinuity at the wall is negligible compared with that at the wire.

Further, since the coefficient γ is proportional to the mean free path, which varies inversely as the pressure, equation (2) may be written

$$W = \frac{2\pi Kl\,(\theta_1 - \theta_2)}{\log_e \frac{r_2}{r_1} + \frac{X}{p}}, \qquad (3)$$

where p is the pressure of the gas and X a constant involving the accommodation coefficient and the mean free path at normal pressure.

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* 'Ann. Physik,' vol. 11, p. 102 (1900).

† 'SitzBer. Akad. Wiss. Wien,' vol. 108, p. 5 (1899).

Moreover, if W_0 is the heat loss due to pure conduction—that is, in the absence of temperature discontinuity and accommodation—we have that

$$W_0 = \frac{2\pi K l(\theta_1 - \theta_2)}{\log_e \frac{r_2}{r_1}}, \tag{4}$$

whence on eliminating K from equations (3) and (4) we obtain an equation which can be written in the form

$$\frac{1}{W} = \frac{X}{W_0\, p \log_e \frac{r_2}{r_1}} + \frac{1}{W_0}, \tag{5}$$

Hence plotting $1/W$ against $1/p$ a straight line should result assuming convective heat losses to be absent. The intercept on the inverse wattage axis will correspond to the true heat conduction, from which the thermal conductivity of the gas may be determined.

Typical examples of these lines are shown in fig. 1. For the heavier gases, it will be seen that the lines fall off at the higher pressures indicating the presence of convection. Thus from the experimental data alone it is possible, at one and the same time, to eliminate the three important errors which arise in the determination of heat conduction through gases.

It is important to note that the absolute value of the thermal conductivity is independent of the form of the coefficient γ, other than the assumption that γ is proportional to the mean free path and therefore varies inversely as the pressure, a supposition which has been established experimentally by Kundt and Warburg.

Assuming a value of the mean free path, which may be calculated from Meyer's relation

$$\lambda = \frac{\eta\pi\sqrt{2\pi}}{4\sqrt{p\rho}},$$

where η is the viscosity, p the pressure in dynes/cm.^{2} and ρ the density in grams/c.c., a knowledge of the slopes of the lines enables the accommodation coefficients to be evaluated for different temperatures of the wire.

Before the final value of the thermal conductivity of the gas can be determined it is necessary to know the temperature of the inner surface of the glass tube. This may be calculated for any rate of heat loss from the wire from the equation

$$\frac{C^2R}{J} = \frac{2\pi K_g l\theta_2}{\log_e \frac{r_3}{r_2}},$$

where r_2 is the external radius of the tube and K_g the thermal conductivity of "pyrex." The latter has recently been accurately determined by Mr. R. W. B. Stephens, of the Imperial College, over a range of temperatures of 500° C. The value at 0° C. being 0·0025 cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.

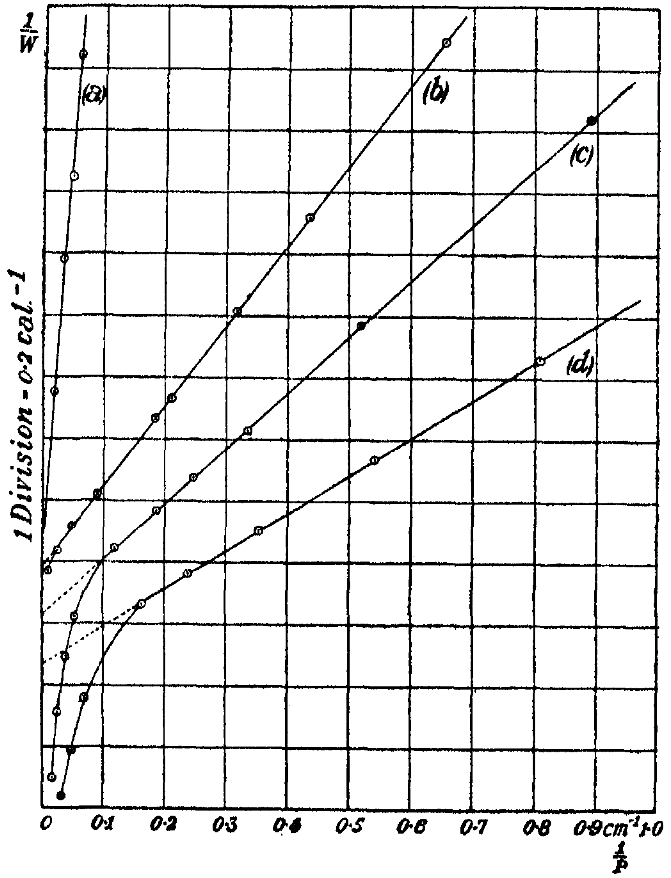

Fig. 1.—Temperature 20° C. (a) hydrogen; (b) oxygen; (c) carbon dioxide; (d) sulphur dioxide.

The Apparatus.

The tubing used for the construction of the experimental tubes was selected from a number of pieces of "pyrex" tubing, the uniformity of which had previously been tested carefully. The selected tube was of small radius (0·3346 cm.) in order to minimize the heat losses due to convection.

In order to enhance the effect of the temperature discontinuity and thus increase the accuracy of the experiment it was necessary to use a platinum wire of small radius (0·003765 cm.) in the tubes, this further had the effect of reducing the radiation correction and increasing the sensitivity of the temperature measurement.

The radius of the tube was found in the usual manner by weighing the quantity of mercury required to fill a known length, while that of the wire was determined by weighing a length of about 300 cm. on an assay balance. Two lengths, giving a difference of 20·09 cm., were then cut and soldered to thick platinum leads and springs and mounted along the axes of the tubes, care being taken that the ends were exactly similar and that the thick leads extended into the uniform part of the tube. While this is essential, the lead wires should be kept as short as possible in order to minimize any convection currents which may be set up owing to the sharp rise of temperature along the thick lead wires. These points are highly important to ensure accurate compensation and a uniform radial distribution of temperature.

The tubes were then securely fixed to a vertical brass mounting fitting into one arm of a U-tube, fixed in a galvanized iron ice-bath containing crushed ice and water; in the other arm of the U-tube was inserted a motor-driven paddle wheel, which forced a copious stream of ice-cold water past the tubes, thus maintaining the external surface of the tubes at a constant temperature of 0° C.

In gaseous connection with the tubes was a mercury manometer, a Toëpler pump for suitably reducing the pressure and a charcoal pocket, used in conjunction with a steel mercury vapour diffusion pump for completely exhausting the apparatus between the observations on different gases, fig. 2.

The scheme of electrical connections is shown in fig. 3. The main and compensating tubes were inserted in the arms of a Callendar and Griffith's bridge, and the current flowing through the wires varied by means of a system of rheostats. In order to determine the current, a standard resistance of 1-ohm was inserted in series with the main tube, and the potential drop across it measured by means of a Crompton potentiometer, a compensating resistance of 1-ohm was inserted in the opposite arm so that the mid-point of the bridge would not be too greatly altered.

The success of the method depends entirely on the accurate measurement of the variation of wattage loss with pressure at a constant temperature of the wire. By no means, other than a bridge system, is it possible to maintain the temperature of the wire accurately constant during a series of observations, since a reduction of the gas pressure necessitates an adjustment of the current strength, which is effected by a variation of resistance in the battery circuit.

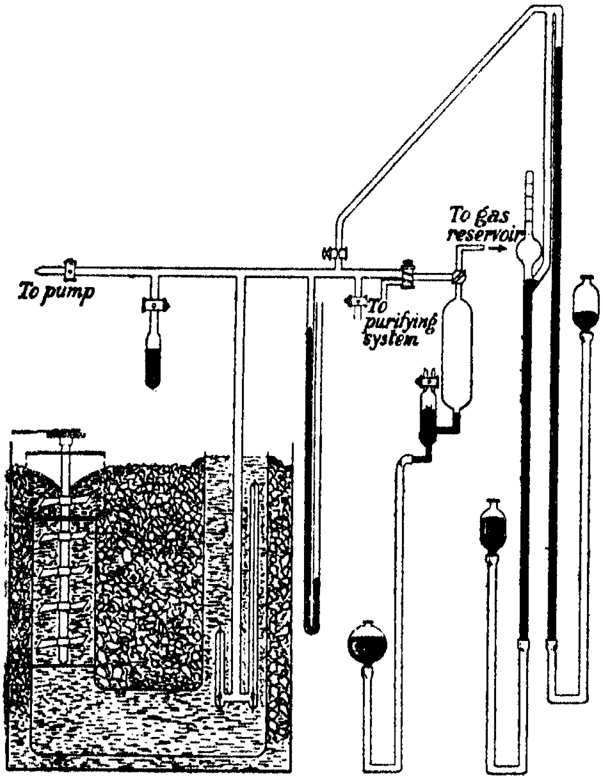
To pump
To gas reservoir
To purifying system

FIG. 2.

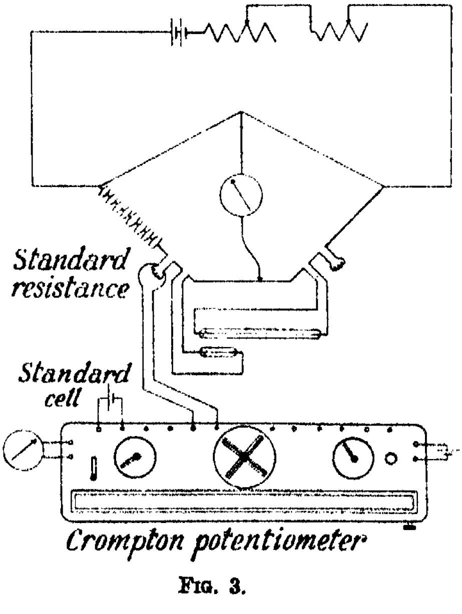
Standard resistance
Standard cell
Crompton potentiometer

FIG. 3.

Helium and hydrogen, which are associated with a large temperature drop effect, small accommodation coefficient, and in which convective heat losses are negligible, necessitate current measurements only in the region of pressures between 76 cm. and 10 cm. of mercury, as the current required to balance the bridge decreases very rapidly as the pressure is reduced. For this region a mercury manometer is sufficiently accurate to measure the pressure. However, for the other gases investigated, in which the discontinuity effect is not nearly so marked, the current does not decrease appreciably until the pressure is reduced to about 10 cm., further with the heavier gases convection was found to persist to a pressure of about 15 cm.

It was found that a mercury manometer was not satisfactory for measuring pressures of this order to the degree of accuracy required in the present experiment. It was therefore necessary to design a gauge suitable for measuring pressures in the desired range, namely, from 10 cm. to 1 cm. of mercury.

The gauge designed was a type of McLeod, in which about 15 c.c. of the gas were isolated and the pressure required to compress this volume to a known smaller volume could be determined. The construction of the gauge is shown in fig. 2, the volumes to the different marks on the side tube were accurately determined before the gauge was assembled.

To measure the pressure, which is known approximately from the manometer, a quantity of the gas is isolated in the gauge by means of the tap and a known volume V compressed to any convenient volume in the upper stem. To compensate for the change in pressure above the mercury in the side tube through raising the reservoir, a second reservoir, connected to another tube of equal cross-section in gaseous connection and running parallel to the first tube, is lowered a corresponding amount. Thus the total volume of gas in the gauge, other than that in the bulb itself, therefore remains constant.

If p is the pressure to be measured and h the difference in levels in the closed and side tube, then

$$pV = (h + p) v$$

whence

$$p = \frac{hv}{V - v},$$

v being the volume to which the gas is compressed.

In the range of pressures used during the investigation of the heavier gases the presence of the compensator is very important, there being a difference of 5% between a measurement of the pressure with and without the use of the compensating tube for the higher pressures. In practice, the volume "v" was always chosen to make "h" as large as possible.

Experimental Procedure.

Before the bridge can be set to any desired temperature it is necessary to know the fundamental interval of the effective length of the wires in the two tubes. This is determined by measuring the effective resistance at the temperatures of steam and melting ice.

The procedure adopted was to insert the tubes in a large hypsometer and measure the resistance for several small currents which were determined by means of the potentiometer. Then, plotting the resistance against the heat developed in the wires, a straight line is obtained and an extrapolation to $C^2R = 0$ gives the true resistance at steam temperature. The resistance at 0° C. was determined in a similar manner with the tubes immersed in the ice-bath.

The fundamental interval having been determined as described above, the resistance corresponding to any temperature θ_{pt} on the platinum scale can be found from the relation

$$\theta_{pt} = \frac{R - R_0}{R_{100} - R_0} \times 100,$$

where R_0 and R_{100} are the resistances at 0° C. and 100° C. respectively.

The temperature θ_{pt} is then converted to the gas scale using Callendar's relation

$$\theta - \theta_{pt} = 1 \cdot 5 \times 10^{-4} (\theta - 100)\, \theta,$$

θ being the temperature on the gas scale.

The method of making the observations in a determination of the thermal conductivity was as follows :—

The bridge having been set to the desired temperature, the gas was allowed to enter the apparatus and the pressure adjusted to any desired value by means of the Toëpler gas recoverer, the levels of the mercury in the pressure gauge being set to two points as shown in fig. 2. The bridge was now balanced and the current determined ; the gauge was isolated from the remainder of the apparatus by means of the tap and the gas in the closed tube compressed to any convenient volume. The height to which the mercury rose in the side tube was noted and the compensating reservoir lowered a corresponding amount, the pressure of the compressed gas then being observed. The current was now redetermined and invariably found to be identical with that previously measured.

A series of observations of current and pressure were taken at the one temperature of the wire as the pressure was reduced. This was repeated for different bridge settings corresponding to different temperatures, the observations, in general, being confined to the region of pressures between 10 cm. and 1 cm. of mercury for the reasons previously stated.

As in a previous research, the ice-point was found to change by small amounts from time to time, it was therefore necessary to determine the ice-point at the conclusion of each set of observations on the conductivity. It was, however, unnecessary to redetermine the fundamental interval, for while a small change in R_0 will affect the value of $R - R_0$ quite appreciably for small values of θ, the percentage change in $R - R_{100}$ is negligible.

Finally, as a check on the constants of the apparatus, a determination of the thermal conductivity of air was made at the conclusion as well as at the commencement of the present research and the values found to agree to 2 in 5000, which is well within the limits of the experimental error.

Preparation of the Gases.

Early experiments in the present investigation showed that it was important that the gas should be thoroughly dried. The steadiness of the galvanometer in the bridge circuit served as a good indication of the quantity of water vapour present in the gas, for it was found that with a damp gas, on reducing the pressure, the current required to balance the bridge for the same temperature exhibited a tendency to creep for some considerable time before assuming a constant value. This was probably due to the condensation of water vapour on the inner wall of the tube and gradual evaporation as the pressure was reduced.

The presence of water vapour, while not changing very appreciably the intercept of the line on the inverse wattage axis, changes the slope of the line quite considerably. If the conductivity of the gas is lower than that of water vapour ($K_0 = 0\cdot0000470$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$), the slope tends to be decreased. Efficient drying of the gas is therefore highly important from the point of view of determining the accommodation coefficient.

The various methods of preparation of the different gases used were carefully considered, and that method which yielded the purest product selected, precautions being taken to remove any possible impurities. It was found possible to reproduce results for the thermal conductivity of all the separate specimens prepared to a consistency of about $0\cdot05\%$.

(1) *Helium.*—This was supplied by the British Oxygen Company in a glass bulb which could be fused on to the apparatus. It was guaranteed to be in a high state of purity.

When the apparatus had been thoroughly evacuated and well baked, the seal was broken and the gas allowed to expand into the apparatus. After a complete set of observations had been obtained, the gas was purified by passing it over heated copper oxide and through charcoal immersed in liquid air.

(2) *Argon.*—This was also supplied by the British Oxygen Company. The gas was purified by passing it over heated copper turnings and magnesium ribbon, condensed and fractionated.

(3) *Hydrogen.*—This was prepared by the action of a concentrated solution of potassium hydroxide on coarse aluminium powder, and purified by passing the gas over heated magnesium to remove traces of oxygen and nitrogen, and through a liquid air trap to remove any condensable impurities.

(4) *Carbon Monoxide.*—A very pure specimen of carbon monoxide may be obtained by the action of pure sulphuric acid on sodium formate, the only likely impurity being carbon dioxide, which is easily removed by passing the gas through a liquid air trap. Several specimens prepared by this method yielded the same value of the conductivity.

(5) *Oxygen.*—The gas was prepared by heating potassium permanganate in a hard glass tube, traces of carbon dioxide being removed by a liquid air trap.

(6) *Air.*—Atmospheric air was used after the removal of dust, carbon dioxide, and water vapour.

(7) *Nitrogen.*—The specimens were prepared by heating a mixture of pure ammonium bichromate and twice its weight of clean fine sand, contained in a hard glass tube. The oxides of nitrogen and water liberated in the reaction were taken up in phosphorus pentoxide tubes and liquid air traps, the last traces of the oxides being reduced to nitrogen by passing the gas over hot copper. The gas was repurified for the second series of observations by again passing it over hot copper.

(8) *Nitrous Oxide.*—The gas may be conveniently obtained in cylinders in a high state of purity. It was, however, considered advisable to liquefy the gas and fractionate it.

Nitrous oxide was also prepared by the action of hydroxylamine hydrochloride on sodium nitrite and purified by fractionation.

(9) *Carbon Dioxide.*—The specimens were prepared by heating pure sodium bicarbonate in a hard glass tube. The large quantity of water liberated being absorbed by phosphorus pentoxide.

The gas was also prepared by the action of pure hydrochloric acid on calcium carbonate.

(10) *Sulphur Dioxide.*—The gas was prepared from liquid sulphur dioxide obtainable in a syphon and the fractionation method of purification used.

(11) *Ammonia.*—The method adopted was to purify cylinder ammonia by successive fractionation, the water vapour present being removed by calcium oxide.

With the last four gases, a large volume of gas was condensed in the first trap, the liquid air removed and the middle fraction collected in a second trap after passing through a drying tube. This was repeated three times, when the preceeding drying tubes were cut off and the apparatus, including the trap containing the solidified gas, evacuated for a considerable time before the liquid air was removed and the gas allowed to enter the reservoir.

After the preliminary set of observations has been obtained, the gas was again condensed, refractionated and the conductivity of the middle fraction determined. The agreement between the two results was always well within the limits of experimental error.

The Results.

The observations on the different gases investigated are embodied in the following tables and curves. A complete tabulation of the results for oxygen is given as representative of the type of readings taken in a determination of the thermal conductivity of any one gas. For the remaining gases the observations at one temperature only are given.

The following is a key to the symbols used in the preceding text and in the tables :—

θ_1 = the temperature of the wire in °C.

θ_2 = the temperature of the inner surface of the wall in °C.

p = the pressure of the gas in centimetres of mercury.

C = the current flowing through the wires in ampères.

R = the effective resistance of the wires in ohms.

J = the mechanical equivalent of heat = 4·184 joules per calorie.

W = the heat loss from the wires in calories corrected for radiation.

W_0 = the heat loss due to pure conduction, *i.e.*, corrected for accommodation and temperature discontinuity.

l = the effective length of the wire = 20·09 cm.

r_1 = the radius of the wire = 0·003765 cm.

r_2 = the internal radius of the tubes = 0·3346 cm.

r_3 = the external radius of the tubes = 0·3962 cm.

K = the absolute value of the thermal conductivity of the gas at T° C. in cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.

T = the mean temperature of the wire and inner surface of the wall.

K_0 = the thermal conductivity of the gas at 0° C.

β = the temperature coefficient per deg. C.

a = the accommodation coefficient.

Table II.—Oxygen.

θ_1.	p.	C.	W.	W_0.	θ_2.	K × 10^7.	T.	a.
23·818	10·10	0·17819	0·040674	0·040964	0·021	611·6	11·92	0·90
	5·03	0·17752	0·040373					
	3·06	0·17673	0·040009					
	2·24	0·17598	0·039669					
	1·73	0·17519	0·039313					
	1·18	0·17347	0·038541					
19·778	10·20	0·16306	0·033615	0·033843	0·017	608·2	9·90	0·90
	4·98	0·16242	0·033350					
	4·17	0·16218	0·033252					
	3·02	0·16167	0·033042					
	2·32	0·16115	0·032892					
	1·60	0·16007	0·032390					
15·743	10·75	0·14597	0·026582	0·026761	0·014	604·5	7·88	0·90
	5·00	0·14548	0·026403					
	3·82	0·14510	0·026265					
	3·15	0·14483	0·026167					
	2·27	0·14427	0·025965					
	1·52	0·14320	0·025580					
11·714	11·49	0·12644	0·019684	0·019798	0·010	600·6	5·86	0·90
	5·08	0·12595	0·019531					
	4·03	0·12571	0·019457					
	2·93	0·12532	0·019336					
	2·30	0·12495	0·019222					
	1·64	0·12432	0·019001					
7·690	9·01	0·10273	0·012822	0·012922	0·006	597·0	3·85	0·90
	5·03	0·10244	0·012749					
	3·94	0·10224	0·012699					
	2·89	0·10194	0·012624					
	2·67	0·10184	0·012600					
	1·85	0·10129	0·012464					

K_0 = 0·0000590 cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.

β = 0·0030 per deg. C.

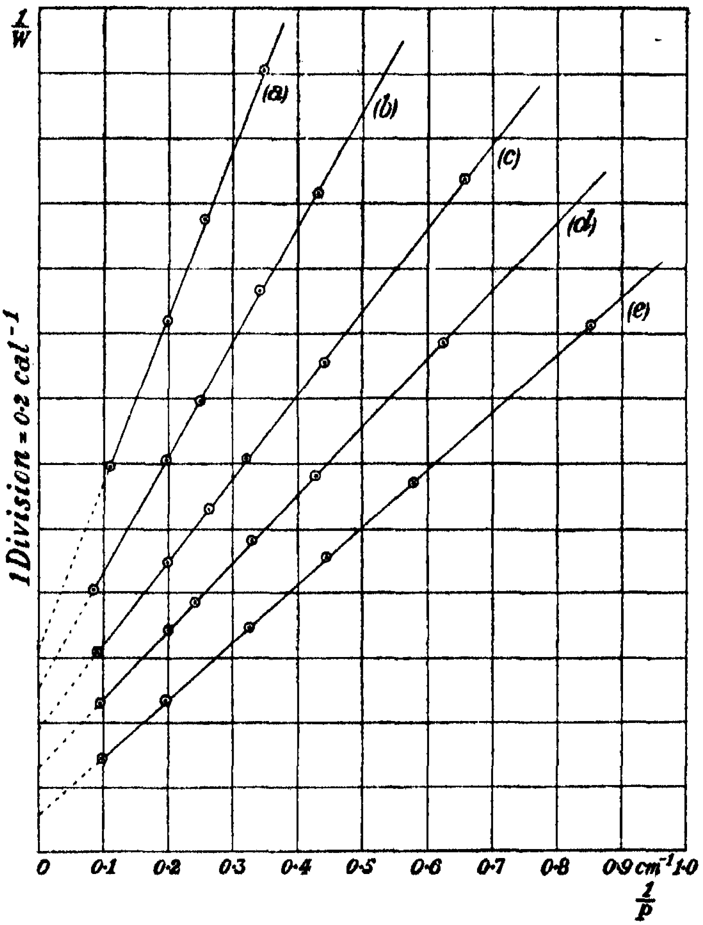

FIG. 4.—Oxygen. (*a*) 7·69° C.; (*b*) 11·71° C.; (*c*) 15·74° C.; (*d*) 19·78° C.; (*e*) 23·82° C.

Table III.

Gas.	θ_1.	*p*.	C.	W.	W_0.	θ_2.	K × 10^7.	T.	*a*.
He	23·194	77·43 44·94 29·51 20·71 15·40 11·10	0·42514 0·42432 0·42295 0·42153 0·41974 0·41724	0·23162 0·23062 0·22923 0·22769 0·22576 0·22308	0·23311	0·119	3591	11·66	0·51
A	23·852	5·78 3·95 2·66 2·15 1·39 0·76	0·14555 0·14508 0·14441 0·14397 0·14268 0·13961	0·027098 0·026923 0·026673 0·026510 0·026035 0·024922	0·027465	0·018	409·5	11·93	0·88

Table III—(continued).

Gas.	θ_1.	p.	C.	W.	W_0.	θ_2.	$K \times 10^7$.	T.	a
H_2	17·976	62·50	0·41172	0·21323	0·21494	0·110	4277	9·04	0·35
		44·20	0·41108	0·21258					
		30·23	0·41000	0·21145					
		22·99	0·40895	0·21038					
		16·82	0·40737	0·20875					
		12·98	0·40557	0·20692					
CO	23·846	7·63	0·17296	0·038316	0·038718	0·020	577·7	11·93	0·91
		4·72	0·17265	0·038178					
		3·39	0·17225	0·038000					
		2·57	0·17169	0·037754					
		1·79	0·17078	0·037353					
		1·11	0·16891	0·036537					
Air	23·852	9·17	0·17716	0·040207	0·040518	0·020	604·4	11·94	0·90
		5·21	0·17665	0·039974					
		3·13	0·17584	0·039608					
		2·23	0·17507	0·039260					
		1·71	0·17428	0·038907					
		1·19	0·17281	0·038251					
N_2	23·813	9·35	0·17666	0·039978	0·040271	0·020	601·6	11·92	0·90
		4·90	0·17608	0·039714					
		3·98	0·17583	0·039601					
		2·72	0·17514	0·039291					
		2·05	0·17442	0·038968					
		1·10	0·17205	0·037911					
N_2O	23·796	7·25	0·14147	0·025593	0·025741	0·013	384·7	11·90	0·90
		4·65	0·14119	0·025491					
		4·05	0·14109	0·025456					
		2·92	0·14078	0·025343					
		1·98	0·14027	0·025158					
		1·18	0·13921	0·024778					
CO_2	23·813	8·33	0·13874	0·024610	0·024729	0·013	369·4	11·91	0·92
		5·35	0·13852	0·024532					
		4·05	0·13833	0·024465					
		2·97	0·13807	0·024372					
		1·92	0·13751	0·024173					
		1·11	0·13641	0·023787					
NH_3	23·829	7·58	0·16926	0·036732	0·036970	0·019	551·9	11·93	0·88
		4·98	0·16902	0·036584					
		3·52	0·16870	0·036446					
		2·55	0·16823	0·036241					
		1·68	0·16740	0·035874					
		1·25	0·16652	0·035507					
SO_2	37·757	6·06	0·13269	0·023436	0·023535	0·012	221·6	18·89	0·95
		4·20	0·13253	0·023378					
		2·81	0·13233	0·023308					
		1·83	0·13199	0·023203					
		1·24	0·13154	0·023018					
		0·92	0·13090	0·022802					

In the preceding tables the temperature of the wire has been expressed to 0·001° C. Actually these temperatures are only correct to 0·005° C., as the fundamental interval of the experimental system was 1·7476 ohms. The temperature measurement of the wire has been expressed to this degree of accuracy to allow for the small fall in temperature across the wall of the tube. It should be realized, however, that while the temperature can only be measured to 0·005° C. the sensitivity of the galvanometer in the bridge circuit is such that a much smaller change of temperature can be readily detected

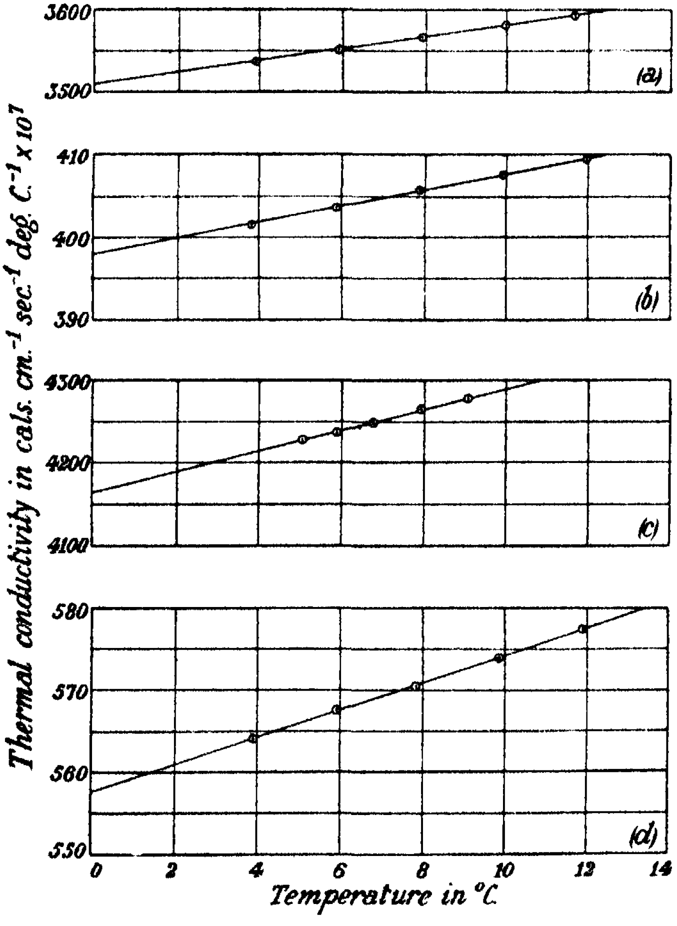

FIG. 5.—(*a*) Helium : $K_0 = 0{\cdot}0003510$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0{\cdot}0021$ per deg. C.
(*b*) Argon : $K_0 = 0{\cdot}0000398$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0{\cdot}0025$ per deg. C.
(*c*) Hydrogen : $K_0 = 0{\cdot}0004170$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0{\cdot}0028$ per deg. C.
(*d*) Carbon monoxide : $K_0 = 0{\cdot}0000558$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0{\cdot}0029$ per deg. C.

and the control is such that the temperature can be maintained constant to 0·001° C.

In determining the temperature of the inner surface of the glass tube, it has been assumed that the external surface is at the temperature of the bath,

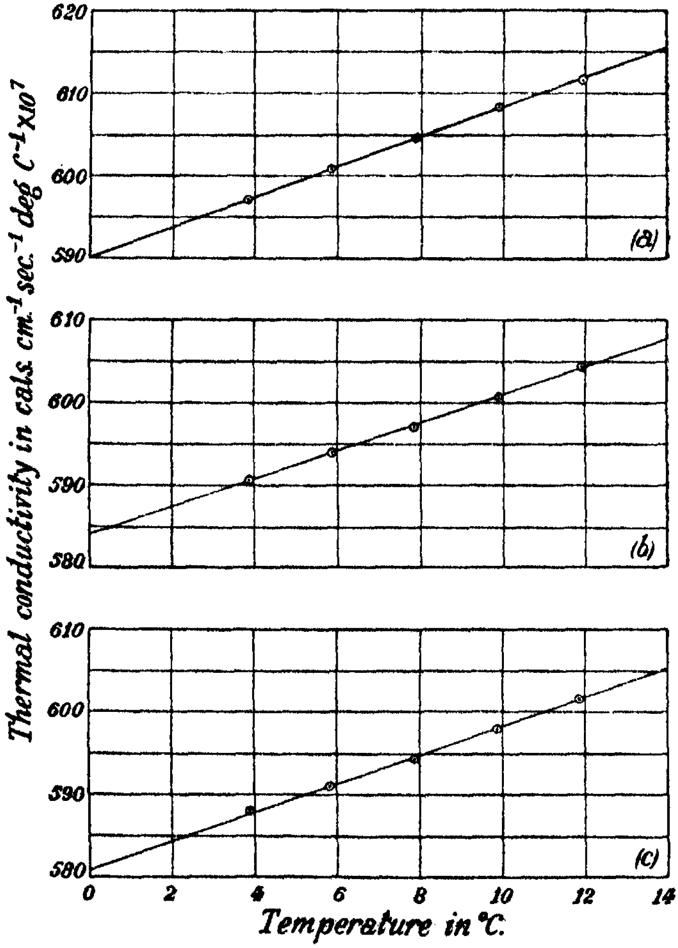

Fig. 6.—(a) Oxygen : $K_0 = 0·0000590$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0·0030$ per deg. C.
(b) Air : $K_0 = 0·0000584$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0·0029$ per deg. C.
(c) Nitrogen : $K_0 = 0·0000581$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0·0029$ per deg. C.

namely, 0° C. This assumption has received experimental verification by Gregory, who, using the same thermostatic system under the same experimental conditions, measured the temperature of the external surface of the tube. His results show that the temperature of the outside wall, with a current of

0·4 amp. flowing through the wires, is identical with that when no current is flowing.

The Crompton potentiometer, which had been previously calibrated by Crompton's, enables the current to be determined to the fourth decimal place, with an estimation of the fifth figure, making use of galvanometer deflections. However, since thermo-e.m.f's are likely to be of this order, a determination of the current was therefore made on reversal; in no test did the two

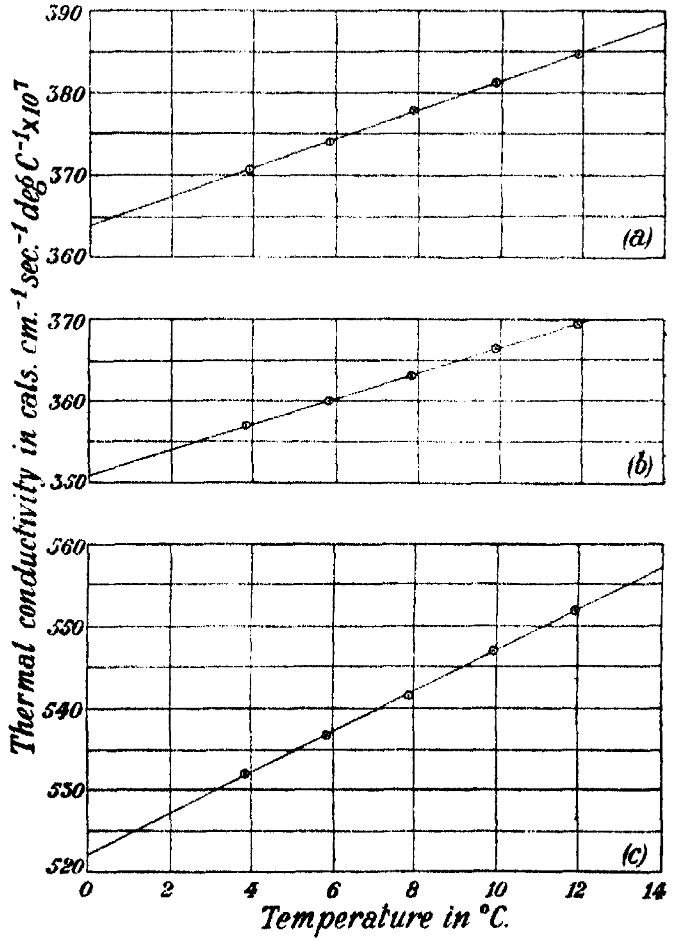

FIG. 7.—(*a*) Nitrous oxide: $K_0 = 0{\cdot}0000364$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0{\cdot}0047$ per deg. C. (*b*) Carbon dioxide: $K_0 = 0{\cdot}0000351$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0{\cdot}0047$ per deg. C. (*c*) Ammonia: $K_0 = 0{\cdot}0000522$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; [illegible] $= 0{\cdot}0048$ per deg. C.

readings differ by more than 0·00004 amp. For the purpose of estimating the resultant accuracy of the experiment, a possible error of this order has been assumed.

A knowledge of the density of platinum is necessary in order to calculate the radius of the wire, the possibility of a change in density with drawing has been considered. The effect of a change in density of 0·5%, however, only introduces an error of 0·15% in the conductivity.

The resultant accuracy of the thermal conductivity can be readily estimated in terms of the accuracy of the various measured quantities involved in the formula for the heat conduction through the gas.

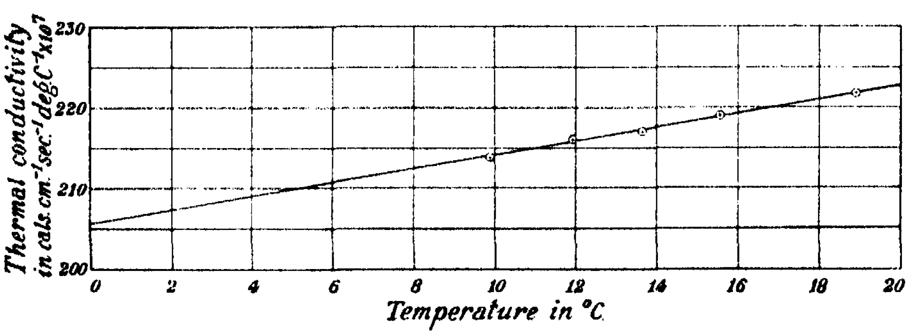

FIG. 8.—Sulphur dioxide: $K_0 = 0·0000206$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$; $\beta = 0·0039$ per deg. C.

For oxygen at 20° C., assuming a possible error of 0·00004 amp. in the current measurement and an error of 0·01 cm. in the bridge setting, the percentage error in K is 0·07%. A further error of 0·01 cm. in the measurement of the effective length of wire in the tubes, which was determined by means of a travelling microscope, would introduce an additional error of 0·05%, while the error in $\log_e \frac{r_2}{r_1}$ at a conservative estimate is not more than 0·2%.

The sum of the individual errors yields a maximum error of 0·32% in the conductivity at 20° C. and similarly at the lowest temperature used, namely, 8° C., the accuracy has been estimated to be 0·39%.

It will be seen from the preceding estimation that the main errors occur in the measurement of the dimensions of the apparatus, rather than in the actual determination of the current and resistance; hence the comparative accuracy of the results as a whole is considerably greater than 0·4%, a point which has been made evident by the ease with which the values of the conductivity could be reproduced for different pure specimens of the same gas.

Discussion of the Results.

The results obtained for the thermal conductivity of gases by previous observers show a very wide deviation from the mean, the variation sometimes amounting to as much as 10%. This may be reasonably attributed to the difficulty in disentangling the effect of pure conduction from those of convection and radiation.

However, for the purpose of comparison the results obtained in the present research and the mean of those obtained by previous investigators, at 0° C., are shown in Table IV.

Table IV.

Gas.	Thermal conductivity at 0° C. cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.		Temperature coefficient per deg. C.	
	Present experiment.	Previous mean.	Present experiment.	Previous mean.
He	0·0003510	0·0003381	0·0021	0·0032
A	0·0000398	0·0000388	0·0025	0·0026
H_2	0·0004170	0·0004037	0·0028	0·0030
CO	0·0000558	0·0000537	0·0029	0·0040
O_2	0·0000590	0·0000576	0·0030	0·0029
Air	0·0000584	0·0000571	0·0029	0·0024
N_2	0·0000581	0·0000571	0·0029	0·0029
N_2O	0·0000364	0·0000356	0·0047	0·0037
CO_2	0·0000351	0·0000339	0·0047	0·0031
SO_2	0·0000206	0·0000195	0·0039	—
NH_3	0·0000522	0·0000514	0·0048	—

In determining the mean values given in Table IV, those values obtained by investigators which deviate by more than 5% from the mean have been neglected, even so it will be seen that the differences are quite appreciable and the present values are always higher.

Measurements made using the "hot-wire" method have invariably been higher than those obtained by either the "plate" or "cooling thermometer" methods, hence such deviations are to be expected. However, if the results are compared with those obtained from the "hot-wire" method alone, the agreement is considerably better. To mention but one example, that of air. The mean value of all measurements on the thermal conductivity of air during the last 20 years is 571×10^{-7} cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$, whereas the mean of the determinations made using the "hot-wire" method is 579×10^{-7}.

The value obtained for air in the present research, 584×10^{-7}, is of particular interest, in view of the fact that in a recent paper on the thermal conductivity of the rare gases by Curie and Lepape* the apparatus was calibrated using a value of 583 $\times 10^{-7}$ for the thermal conductivity of air, obtained by Gregory and Archer, as a standard. The "cooling thermometer" method was used and the values found for helium and argon are in good agreement with those obtained by the author.

The values found for the monatomic gases, helium and argon, are interesting in view of the theoretical relation between the thermal conductivity K, the viscosity η, and the specific heat at constant volume C_v, the values obtained for the ratio $K/\eta C_v$ for helium and argon are 2·50 and 2·52 respectively.

With regard to the accommodation coefficients, the only available data is due to Knudsen, whose values were obtained from observations on the heat conduction through rarefied gases.† The results are compared with those of the author in Table V.

Table V.

Gas.	Accommodation coefficient.	
	Knudsen.	Dickins.
He	0·34	0·50
A	0·86	0·89
H_2	0·36 0·28	0·36
CO	—	0·92
O_2	0·84	0·90
Air	—	0·90
N_2	0·87	0·89
N_2O	0·73	0·89
CO_2	0·86	0·91
NH_3	—	0·87
SO_2	—	0·96

It will be observed that the values are in quite good agreement, considering the fact that the accommodation coefficients have been determined under very different experimental conditions. Further, it is important to note that the accommodation coefficient depends very largely on the condition of the surface of the wire at the time of the experiment. It has been shown by Roberts‡ that the accommodation coefficient for hydrogen for a freshly flashed tungsten wire increases to six times its original value in a few seconds as the wire becomes contaminated with the gas.

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* 'J. Phys. Rad.,' vol. 7, p. 392 (1931).

† 'Ann. Physik,' vol. 40, p. 492 (1913).

‡ 'Proc. Roy. Soc.,' A, vol. 129, p. 146 (1930).

In the present work, however, we are not so much concerned with absolute values as with the elimination of the effect of accommodation on the measurement of heat conduction through gases.

Conclusion.

It is hoped that the present work has led to more definite data in relation to heat conduction through gases, in view of the fact that the important errors arising in such a determination by the "hot-wire" method have been reduced to a minimum and, further, have been eliminated in one operation by purely experimental means.

In conclusion, the author wishes to thank Professor G. P. Thomson for the facilities placed at his disposal; he also has much pleasure in recording his gratitude to Professor H. S. Gregory for his constant interest and helpful advice given during the course of the work.

Summary.

The present paper describes a modification of the "hot-wire" method for determining the thermal conductivity of a gas. The inherent errors due to convection, the effect of accommodation, and the temperature discontinuity between the gas and solid surfaces surrounding the gas are eliminated by experimental means in one operation, while the radiation correction is very small.

It can be shown theoretically that the heat conduction across a gas under the cylindrical distribution of temperature may be represented by

$$W = \frac{2\pi K l \theta}{\log_e \frac{r_2}{r_1} + \frac{X}{P}}$$

where K is the thermal conductivity of the gas, l and r_1 the length and radius of the wire, r_2 the radius of the coaxial cylinder containing the gas and θ the temperature difference across the gas. The term X/P is a correction due to the effect of accommodation and temperature discontinuity, which depends on the pressure, P.

The equation may be written in the form

$$\frac{1}{W} = \frac{1}{W_0} + \frac{Y}{P},$$

where W_0 is the heat conduction in the absence of accommodation, temperature discontinuity and convection, hence by plotting $1/W$ against $1/P$ a straight line should be obtained, provided there is no convection.

This law was found to hold below certain pressures for all the gases investigated. The pressure above which the law no longer holds being lower, the heavier the gas, in accordance with the fact that convective heat losses increase with molecular weight.

The thermal conductivity and the accommodation coefficients, which can be found from the intercepts and slopes of the lines so obtained, have been determined for eleven gases.

Spark Spectra of Bismuth, Bi III and Bi II.

By M. F. Crawford and A. B. McLay.*

(Communicated by Professor J. C. McLennan, F.R.S.—Received September 7, 1933.)

Term schemes for Bi III and Bi II were established by the authors† in 1930. A few terms in each spectrum were found to have large hyperfine structure separations. Later Fisher and Goudsmit‡ carried out an experimental and theoretical study of the hyperfine structures of these spectra which, in general, confirmed our term analyses. In the present communication we report the results of a more extended investigation of the term structures of these two spectra, and in addition give further information on their hyperfine structures.

New experimental data were obtained by photographing spectra of bismuth from 1000 A. to 10,000 A. For the extreme ultra-violet region a vacuum spectrograph, designed and set up by one of us (M. F. C.), was used. Equipped with a 2-metre N.P.L. grating, this spectrograph has an average dispersion of 8·75 A. per millimetre. A Hilger E_1 quartz spectrograph was employed to investigate the near ultra-violet and visible regions; and a Hilger constant deviation spectrograph for the infra-red.

The spectra were excited by an electrodeless discharge in bismuth vapour. The source consisted of a quartz tube with an exciting coil wound about its middle section. Metallic bismuth, introduced into the tube, was vapourized by an electric oven. The tube was placed in the oven with the two ends protruding, so that only the middle section carrying the exciting coil was heated. The pressure of the bismuth vapour was controlled by regulating the temperature of the oven. Condensation on the walls of the protruding portions of the tube prevented the quartz windows from becoming coated. When used with the vacuum grating spectrograph, one end of the tube was left open and attached by a taper to the slit of the instrument. In this case also, condensation prevented the vapour from diffusing on to the slit and into the spectrograph.

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* Assistant Professor of Physics, McMaster University, Hamilton, Canada.

† McLennan, McLay, and Crawford, 'Proc. Roy. Soc.,' A, vol. 129, p. 579 (1930).

‡ 'Phys. Rev.,' vol. 37, p. 1057 (1931).

The chief advantages of this source are as follows: firstly, lines of Bi I, II, III, IV,* and even Bi V, can be easily excited and differentiated by observing their behaviour when the vapour pressure and the exciting circuit are varied; secondly, the individual components of complex lines are narrow enough to permit hyperfine structure measurements—not the intrinsic widths of the components but the resolving powers of the spectrographs limited the resolution in this investigation.

A number of plates were taken with the vacuum spectrograph, each with a different excitation condition in the source. Inspection of the intensities of a given line on the various plates usually showed very definitely in which ion of bismuth it originated. For the region above 2000 A. spectrograms of the source were taken under only one excitation condition, which was so chosen as to give Bi II, III, and IV* lines with good average intensity. Variable excitation was not used since the excitation characteristics of the majority of the lines in this region had been determined in our previous investigation.

All lines between 1000 A. and 2000 A. and all those above 2000 A. not previously observed, were measured. The wave-lengths of prominent carbon, nitrogen, oxygen, and mercury lines, which appeared on the plates, served to check the accuracy of our measurements. In general, our wave numbers are estimated to be reliable to within 1 or 2 cm.$^{-1}$. This accuracy is adequate for these term analyses, and is as good as can be expected since most of the lines have some unresolved hyperfine structure. The hyperfine structure intervals given in the tables, however, are more accurate than the absolute values of the wave numbers.

In addition to our data Arvidsson's† measurements, which extend from 1486 A. to 175 A., have been used to advantage. Our values agree very well with his in the region 1486 A. to 1000 A. where they overlap. In view of this and the fact that Arvidsson's measurements alone were available for the region below 1000 A., the wave-lengths of all lines below 1486 A., except a few faint ones observed for the first time by us, were taken from his table. Arvidsson also gave excitation classification of many of the lines observed by him. A comparison of his excitation observations and ours, in the region where they overlap, showed that ours are somewhat more critical, particularly for fainter lines. The analyses of Bi II and Bi III confirm this, since they are quite consistent with our excitation data.

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* Bi IV has been analysed by the authors, and will be published soon.

† 'Ann. Physik,' vol. 12, p. 787 (1932)

The present knowledge of the term and the hyperfine structures of Bi III and Bi II is presented in the following term and classified wave-length tables. Our previous term analyses, in so far as they were developed, were confirmed by the present investigation, except that one term of Bi III and two of Bi II were found to be unreal.

The results for Bi III are summarized in Tables I and II. In the single-electron spectrum the important deepest term $6p\ ^2P_{\frac{1}{2}}^0$ and some higher members of several doublet series have been newly established. The $7d\ ^2D_{2\frac{1}{2}}$ term has

Table I.—Terms of Bi III.

Term.			Value cm.$^{-1}$.	$n.$*	Total Hfs interval cm.$^{-1}$.	Term.		Value cm.$^{-1}$.	$n.$* effective quantum number.
	$6p$	$^2P_{\frac{1}{2}}^0$	0[†]	2·18	—	$7d$	$^2D_{1\frac{1}{2}}$	149086	4·16
	$6p$	$^2P_{1\frac{1}{2}}^0$	20788	2·31	—	$7d$	$^2D_{2\frac{1}{2}}$	149796	4·18
$6s6p_{\frac{1}{2}}$	$6p_{\frac{1}{2}}$	$4_{\frac{1}{2}}$	70254	—	10	$8p$	$^2P_{\frac{1}{2}}^0$	154198	4·35
$6s6p_{\frac{1}{2}}$	$6p_{1\frac{1}{2}}$	$1_{1\frac{1}{2}}$	83038	—	7·5[§]	$8p$	$^2P_{1\frac{1}{2}}^0$	156421	4·45
$6s6p_{\frac{1}{2}}$	$6p_{1\frac{1}{2}}$	$2_{2\frac{1}{2}}$	89236	—	12·5[§]	$6f$	$^2F_{3\frac{1}{2}}^0$	162186	4·738
	$7s$	$^2S_{\frac{1}{2}}$	95075	2·98	2·36[§]	$6f$	$^2F_{2\frac{1}{2}}^0$	162242	4·741
	$6d$	$^2D_{1\frac{1}{2}}$	96154	3·00	—[‖]	$5g$	$^2G_{4\frac{1}{2}}$	166234	4·97
	$6d$	$^2D_{2\frac{1}{2}}$	102446	3·09	—[‖]	$5g$	$^2G_{3\frac{1}{2}}$	166237	4·97
$6s6p_{\frac{1}{2}}$	$6p_{1\frac{1}{2}}$	$5_{\frac{1}{2}}$	108052	—	4	$9s$	$^2S_{\frac{1}{2}}$	167289	5·04
$6s6p_{\frac{1}{2}}$	$6p_{1\frac{1}{2}}$	$6_{1\frac{1}{2}}$	108586	—	—[‖]	$8d$	$^2D_{1\frac{1}{2}}$	169292	5·18
$6s6p_{1\frac{1}{2}}$	$6p_{1\frac{1}{2}}$	$3_{2\frac{1}{2}}$	116414	—	9·3[§]	$8d$	$^2D_{2\frac{1}{2}}$	169657	5·20
	$7p$	$^2P_{\frac{1}{2}}^0$	116993	3·33	0·52[§]	$6g$	$^2G_{4\frac{1}{2}}$	178467	5·97
	$7p$	$^2P_{1\frac{1}{2}}^0$	122128	3·43	0·31[§]	$6g$	$^2G_{3\frac{1}{2}}$	178470	5·97
$6s6p_{1\frac{1}{2}}$	$6p_{1\frac{1}{2}}$	$7_{1\frac{1}{2}}$	130966	—	- 5	$6h$	$^2H^0$	178719	6·00
$6s6p_{1\frac{1}{2}}$	$6p_{1\frac{1}{2}}$	$8_{\frac{1}{2}}$	130986[‡]	—	10	$7g$	$^2G_{4\frac{1}{2}}$	185850	6·97
	$5f$	$^2F_{3\frac{1}{2}}^0$	137455	3·791	—	$7g$	$^2G_{3\frac{1}{2}}$	185853	6·97
	$5f$	$^2F_{2\frac{1}{2}}^0$	137555	3·794	—	$7h$	$^2H^0$	186024[¶]	7·00
	$8s$	$^2S_{\frac{1}{2}}$	145227	4·02	—	$8g$	$^2G_{4\frac{1}{2}}$	190642	7·97
						$8g$	$^2G_{3\frac{1}{2}}$	190644	7·97

[†] The value of this term relative to $6s^2\ ^1S_0$ of Bi IV is 206180 cm.$^{-1}$.

[‡] This term is not as well established as the others.

[§] See Fisher and Goudsmit (*loc. cit.*).

[‖] Breadths of lines involving these terms indicate the terms have hyperfine structure separations of 2 to 3 cm.$^{-1}$.

[¶] This term assumed hydrogenic for the calculation of the limit in † and of the n* values in Table I.

Table II.—Classified Wave-lengths of Bi III.

Intensity.		λ (I.A.).	ν.	Classification.
Arvidsson.	Crawford and McLay.			
—	20	8934	11190	$8s\,{}^2S_{\frac12} - 8p\,{}^2P_{1\frac12}^0$
—	15	8671	11530	$5f\,{}^2F_{2\frac12}^0 - 7d\,{}^2D_{1\frac12}$
—	2	8168	12240	$5f\,{}^2F_{2\frac12}^0 - 7d\,{}^2D_{2\frac12}$
—	20	00	12342	$5f\,{}^2F_{3\frac12}^0 - 7d\,{}^2D_{2\frac12}$
—	50	8070	12388	$7d\,{}^2D_{2\frac12} - 6f\,{}^2F_{3\frac12}^0$
—	5	32	12446	$7d\,{}^2D_{2\frac12} - 6f\,{}^2F_{2\frac12}^0$
—	40	08	12484	$5g\,{}^2G - 6h\,{}^2H^0$
—	10*b*	7637*	13090	$8p\,{}^2P_{\frac12}^0 - 9s\,{}^2S_{\frac12}$
—	25	7598	13157	$7d\,{}^2D_{1\frac12} - 6f\,{}^2F_{2\frac12}^0$
—	12	51	13240	$8p\,{}^2P_{1\frac12}^0 - 8d\,{}^2D_{2\frac12}$
—	10*b*	7381*	13545	$6_{1\frac12} - 7p\,{}^2P_{1\frac12}^0$
—	12	6623·4	15094	$8p\,{}^2P_{\frac12}^0 - 8d\,{}^2D_{1\frac12}$
—	5	6160·6	16228	$6f\,{}^2F_{2\frac12}^0 - 6g\,{}^2G_{3\frac12}$
—	6	6140·4	16281	$6f\,{}^2F_{3\frac12}^0 - 6g\,{}^2G_{4\frac12}$
—	1	39·2	16284	$6f\,{}^2F_{3\frac12}^0 - 6g\,{}^2G_{3\frac12}$
—	45B	5079·3	19682	$6d\,{}^2D_{2\frac12} - 6p\,{}^2P_{1\frac12}^0$
—	3	52·3	19787	$5g\,{}^2G_{3\frac12} - 7h\,{}^2H^0$
—	4	51·7	19790	$5g\,{}^2G_{4\frac12} - 7h\,{}^2H^0$
—	40*b*	4797·4	20839	$6d\,{}^2D_{1\frac12} - 7p\,{}^2P_{\frac12}^0$
—	8	4752·09‖	21037·5	$3_{3\frac12} - 5f\,{}^2F_{3\frac12}^0$
—	6	51·48	21040·2	
—	5	50·96	21042·5	
—	4	50·50	21044·5	
—	3	50·12	21046·2	
—	—	—*	—	
—	3	29·53	21137·9	$3_{2\frac12} - 5f\,{}^2F_{2\frac12}^0$
—	2	28·95	21140·4	
—	2	28·46	21142·6	
—	1	28·02	21144·6	
—	2*b*	27·5	21147	
—	30	4561·54‖	21916·3	$7s\,{}^2S_{\frac12} - 7p\,{}^2P_{\frac12}^0$
—	30	60·84	21919·7	
—	25	4327·8	23100	$7p\,{}^2P_{1\frac12}^0 - 8s\,{}^2S_{\frac12}$
—	5	07·4	23209	$8_{\frac12} - 8p\,{}^2P_{\frac12}^0$
—	5	05·4*	23220	
—	10	4234·1	23611	$6f\,{}^2F_{2\frac12}^0 - 7g\,{}^2G_{3\frac12}$
—	12	24·6	23664	$6f\,{}^2F_{3\frac12}^0 - 7g\,{}^2G_{4\frac12}$
—	8	3931·1	25431	$8_{\frac12} - 8p\,{}^2P_{1\frac12}^0$
—	7	29·6	25441	
—	2*b*	27·2	25456	$7_{1\frac12} - 8p\,{}^2P_{1\frac12}^0$
—	10	3848·8	25975	$6d\,{}^2D_{1\frac12} - 7p\,{}^2P_{1\frac12}^0$
—	10	3708·4	26958	$7p\,{}^2P_{1\frac12}^0 - 7d\,{}^2D_{1\frac12}$
—	50	3695·68‖	27050·9	$7s\,{}^2S_{\frac12} - 7p\,{}^2P_{1\frac12}^0$
—	50	95·32	27053·6	
—	45	13·4	27667	$7p\,{}^2P_{1\frac12}^0 - 7d\,{}^2D_{2\frac12}$
—	15	3540·8	28234	$7p\,{}^2P_{\frac12}^0 - 8s\,{}^2S_{\frac12}$
—	8	19·9	28402	$6f\,{}^2F_{2\frac12}^0 - 8g\,{}^2G_{3\frac12}$
—	8	13·1	28457	$6f\,{}^2F_{3\frac12}^0 - 8g\,{}^2G_{4\frac12}$
—	35	3485·5	28682	$5f\,{}^2F_{2\frac12}^0 - 5g\,{}^2G_{3\frac12}$
—	40	73·8	28779	$5f\,{}^2F_{3\frac12}^0 - 5g\,{}^2G_{4\frac12}$

b Broad.

B Very broad; hyperfine structure partially resolved but difficult to measure.

* Also classified in Bi II—see Table IV.

† Hyperfine structure measured by Fisher and Goudsmit, *loc. cit.*

‖ Breadths of lines involving these terms indicate the terms have hyperfine structure separations of 2 to 3 cm.$^{-1}$.

Table II—(continued).

Intensity.		λ (I.A.).	ν.	Classification.
Arvidsson.	Crawford and McLay.			
—	5	73·4	28782	$5f\,^2F^0_{3\frac{1}{2}}$—$5g\,^2G_{3\frac{1}{2}}$
—	40*b*	51·0	28969	$6_{1\frac{1}{2}}$—$5f\,^2F^0_{2\frac{1}{2}}$
—	4	3196·6	31274	$7_{1\frac{1}{2}}$—$6f\,^2F^0_{2\frac{1}{2}}$
—	3	96·35	31276·2	
—	3*b*	96·15	31278·6	
—	8	50·0	31737	$5f\,^2F^0_{2\frac{1}{2}}$—$8d\,^2D_{1\frac{1}{2}}$
—	35	15·0	32093	$7p\,^2P^0_{\frac{1}{2}}$—$7d\,^2D_{1\frac{1}{2}}$
—	8	04·5	32202	$5f\,^2F^0_{3\frac{1}{2}}$—$8d\,^2D_{2\frac{1}{2}}$
—	9	3039·86	32886·7	$2_{2\frac{1}{2}}$—$7p\,^2P^0_{1\frac{1}{2}}$
—	7	39·53	32890·3	
—	5	39·25	32893·3	
—	4	39·05	32895·6	
—	3	38·87	32897·4	
—	2	38·72	32899·0	
—	8	2944·46	33952·2	$1_{1\frac{1}{2}}$—$7p\,^2P^0_{\frac{1}{2}}$
—	5	44·20	33955·2	
—	4	43·99	33957·6	
—	3	43·84	33959·3	
—	80B	2855·6	35009	$6d\,^2D_{2\frac{1}{2}}$—$5f\,^2F^0_{3\frac{1}{2}}$
—	30B	47·4	35109	$6d\,^2D_{2\frac{1}{2}}$—$5f\,^2F^0_{2\frac{1}{2}}$
—	3	2557·75	39085·2	$1_{1\frac{1}{2}}$—$7p\,^2P^0_{1\frac{1}{2}}$
—	2	57·53	39088·5	
—	1	57·37	39090·9	
—	1	57·23	39093·1	
—	3	2499·06	40003·0	$3_{2\frac{1}{2}}$—$8p\,^2P^0_{1\frac{1}{2}}$
—	2	98·90	40005·6	
—	2	98·77	40007·7	
—	2*b*	98·6	40010	
—	8	43·3	40916	$5f\,^2F^0_{2\frac{1}{2}}$—$6g\,^2G_{3\frac{1}{2}}$
—	10	2437·6	41012	$5f\,^2F^0_{3\frac{1}{2}}$—$6g\,^2G_{4\frac{1}{2}}$
—	2	37·4	41015	$5f\,^2F^0_{3\frac{1}{2}}$—$6g\,^2G_{3\frac{1}{2}}$
—	75*b*	14·6	41402	$6d\,^2D_{1\frac{1}{2}}$—$5f\,^2F^0_{2\frac{1}{2}}$
—	30	2213·55	45162	$7p\,^2P^0_{1\frac{1}{2}}$—$9s\,^2S_{\frac{1}{2}}$
—	8	2191·7	45613	$6_{1\frac{1}{2}}$—$8p\,^2P^0_{\frac{1}{2}}$
—	6	84·23	45768·3	$3_{2\frac{1}{2}}$—$6f\,^2F^0_{3\frac{1}{2}}$
—	4	84·10	45771·1	
—	3	84·00	45773·2	
—	3	83·92	45774·9	
—	2	83·85	45776·3	
—	2	83·79	45777·6	
—	3	81·58	45824	$3_{2\frac{1}{2}}$—$6f\,^2F^0_{2\frac{1}{2}}$
—	2	81·44	45827	
—	1	81·34	45829	
—	1	81·25	45831	
—	1*b*	81·15	45833	
—	2	66·35	46146	$5_{\frac{1}{2}}$—$8p\,^2P^0_{\frac{1}{2}}$
—	2	66·15	46150	
—	3	39·00	46736	$4_{\frac{1}{2}}$—$7p\,^2P^0_{\frac{1}{2}}$
—	4	38·58†	46745	
—	6	19·60	47164	$7p\,^2P^0_{1\frac{1}{2}}$—$8d\,^2D_{1\frac{1}{2}}$
—	15	03·42	47526	$7p\,^2P^0_{1\frac{1}{2}}$—$8d\,^2D_{2\frac{1}{2}}$

b Broad.
B Very broad; hyperfine structures partially resolved but difficult to measure.
† Merged with another line, probably an impurity line of Zn I.

Table II—(continued).

Intensity.		λ (I.A.).	ν.	Classification.
Arvidsson.	Crawford and McLay.			
—	14	2073·37	48215·2	$2_{2\frac12}$ —$5f\,^2F_{3\frac12}^0$
—	10	73·22	48218·7	
—	8	73·10	48221·5	
—	7	72·99	48224·0	
—	6	72·90	48226·1	
—	5	72·83	48227·8	
—	3	69·91	48296	$5f\,^2F_{2\frac12}^0$ —$7g\,^2G_{3\frac12}$
—	3	69·08	48315·2	$2_{2\frac12}$ —$5f\,^2F_{2\frac12}^0$
—	—	——*	——	
—	2	68·72	48323·6	
—	1	68·63	48325·7	
—	1	68·55	48327·5	
—	4	2065·73	48394	$5f\,^2F_{3\frac12}^0$ —$7g\,^2G_{4\frac12}$
—	20	21·15‡	49460	$6p\,^2P_{1\frac12}^0$— $4_{\frac12}$
—	20	20·75	49470	
		λ (I. vac.)		
—	10	1988·26	50295	$7p\,^2P_{\frac12}^0$ —$9s\,^2S_{\frac12}$
—	2	27·88	51870	$4_{\frac12}$ —$7p\,^2P_{1\frac12}^0$
—	2	27·50	51880	
—	10	12·12	52298	$7p\,^2P_{\frac12}^0$ —$8d\,^2D_{1\frac12}$
—	3	1883·63	53089	$5f\,^2F_{2\frac12}^0$ —$8g\,^2G_{3\frac12}$
—	3	80·23	53185	$5f\,^2F_{3\frac12}^0$ —$8g\,^2G_{4\frac12}$
—	10	63·9	53655	$6_{1\frac12}$ —$6f\,^2F_{2\frac12}^0$
—	8	52·72‡	53975	$6d\,^2D_{2\frac12}$ —$8p\,^2P_{1\frac12}^0$
—	20	34·32	54516	$1_{1\frac12}$ —$5f\,^2F_{2\frac12}^0$
—	3*b*	1722·9§	58042	$6d\,^2D_{1\frac12}$ —$8p\,^2P_{\frac12}^0$
—	20*b*	1691·5*	59120	$7s\,^2S_{\frac12}$ —$8p\,^2P_{\frac12}^0$
—	3	73·98	59738	$6d\,^2D_{2\frac12}$ —$6f\,^2F_{3\frac12}^0$
—	3	59·3	60266	$6d\,^2D_{1\frac12}$ —$8p\,^2P_{1\frac12}^0$
—	3	30·11	61346	$7s\,^2S_{\frac12}$ —$8p\,^2P_{1\frac12}^0$
—	60*b*	06·40	62251	$6p\,^2P_{1\frac12}^0$— $1_{1\frac12}$
—	1	1513·06	66091	$6d\,^2D_{1\frac12}$ —$6f\,^2F_{2\frac12}^0$
—	4*b*	1488·44	67184	$2_{2\frac12}$ —$8p\,^2P_{1\frac12}^0$
10*b*	60*b*	1461·00	68446	$6p\,^2P_{1\frac12}^0$— $2_{2\frac12}$
8	35	23·52	70249	$6p\,^2P_{\frac12}^0$ — $4_{\frac12}$
10	35	23·33	70258	
—	3*b*	1370·86	72947	$2_{2\frac12}$ —$6f\,^2F_{3\frac12}^0$
—	2*b*	62·73	73382	$1_{1\frac12}$ —$8p\,^2P_{1\frac12}^0$
15	60	46·12	74287	$6p\,^2P_{1\frac12}^0$—$7s\,^2S_{\frac12}$
9	40	26·84	75367	$6p\,^2P_{1\frac12}^0$—$6d\,^2D_{1\frac12}$
10	50	1224·64	81657	$6p\,^2P_{1\frac12}^0$—$6d\,^2D_{2\frac12}$
0*b*¶	8*b*	04·28	83037	$6p\,^2P_{\frac12}^0$ — $1_{1\frac12}$
6	15	1145·91	87267	$6p\,^2P_{1\frac12}^0$— $5_{\frac12}$
4	20	39·01	87795	$6p\,^2P_{1\frac12}^0$— $6_{1\frac12}$
8	30	1051·81	95074	$6p\,^2P_{\frac12}^0$ —$7s\,^2S_{\frac12}$
8*b*	50*b*	45·76	95624	$6p\,^2P_{1\frac12}^0$— $3_{2\frac12}$
4	25	39·99	96155	$6p\,^2P_{\frac12}^0$ —$6d\,^2D_{1\frac12}$
6	—	925·48	108052	$6p\,^2P_{\frac12}^0$ — $5_{\frac12}$
7	—	20·93	108586	$6p\,^2P_{\frac12}^0$ — $6_{1\frac12}$
5	—	07·64	110176	$6p\,^2P_{1\frac12}^0$— $7_{1\frac12}$

b Broad.
* Also classified in Bi II—see Table IV.
‡ Merged with Bi I line.
§ Merged with Bi IV line.
¶ Intensity according to Arvidsson, *loc. cit.*

Table II—(continued).

Intensity.		λ (I. vac.)	ν.	Classification.
Arvidsson.	Crawford and McLay.			
1	—	07·51	110192	$6p\,^2P_{1\frac{1}{2}}^0$— $8_{\frac{1}{2}}$
1	—	07·42	110203	
6	—	803·65	124432	$6p\,^2P_{1\frac{1}{2}}^0$—$8s\,^2S_{\frac{1}{2}}$
4	—	775·16	129006	$6p\,^2P_{1\frac{1}{2}}^0$—$7d\,^2D_{2\frac{1}{2}}$
2	—	763·56	130966	$6p\,^2P_{\frac{1}{2}}^0$ — $7_{1\frac{1}{2}}$
2	—	688·56	145231	$6p\,^2P_{\frac{1}{2}}^0$ —$8s\,^2S_{\frac{1}{2}}$
2	—	71·74	148867	$6p\,^2P_{1\frac{1}{2}}^0$—$8d\,^2D_{2\frac{1}{2}}$
5	—	70·76	149085	$6p\,^2P_{\frac{1}{2}}^0$ —$7d\,^2D_{1\frac{1}{2}}$
1	—	590·73	169282	$6p\,^2P_{\frac{1}{2}}^0$ —$8d\,^2D_{1\frac{1}{2}}$ (?)

been re-identified. The original term, which was established with limited data, has not been confirmed in this analysis and has been discarded. The term now identified as $7d\,^2D_{2\frac{1}{2}}$ is adequately supported by its combinations with a number of odd terms. As a result of this change, Lang's earlier classification* of the line $\nu = 27667$ as $7p\,^2P_{1\frac{1}{2}}^0$—$7d\,^2D_{2\frac{1}{2}}$ is confirmed. The $6d\,^2D$ interval is larger than expected from the spin-doublet law. This anomaly in all probability is due to the perturbing effect of the overlapping $6s6p^2$ group of the complex spectrum.

All terms of the complex three-electron configuration $6s6p^2$ have been identified, if the tentative term $8_{\frac{1}{2}}$ is real. The disposition of these terms indicates an intermediate type of coupling, but their hyperfine structure interval factors are fairly consistent with the formulæ for extreme (jj) coupling.† In view of this the nomenclature for (jj) coupling has been used in Table I for the $6s6p^2$ configuration, but its use is not to be interpreted as signifying extreme (jj) coupling.

The hyperfine structures of the $6s6p^2$ terms are discussed with the aid of the following table. The formulæ for the interval factors, listed in the second column, were derived by Goudsmit's method for (jj) coupling. They express the interval factor (A) of each multiplet state in terms of the interaction constants, a_{6s}, $a_{6p}(\frac{1}{2})$, $a_{6p}(1\frac{1}{2})$, which govern the absolute magnitude of the interactions of the valence electrons with the magnetic nucleus ($I = 4\frac{1}{2}$).

The first three terms in the table were discussed by Fisher and Goudsmit (*loc. cit.*), and were used by them to evaluate the interaction constants

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* 'Phys. Rev.,' vol. 32, p. 737 (1928).

† 'Phys. Rev.,' vol. 37, p. 663 (1931).

Term.	A, (*jj*) coupling.	A (obs.).	Interaction constants.
$6s\,6p_{\frac{1}{2}}\,6p_{1\frac{1}{2}}\;1_{1\frac{1}{2}}$	$1/3\,.\,a_{6s} - 1/6\,.\,a_{6p}(\frac{1}{2}) + 5/6\,.\,a_{6p}(1\frac{1}{2})$	0·50	$a_{6s} = 1{\cdot}80$ cm.$^{-1}$
$6s\,6p_{\frac{1}{2}}\,6p_{1\frac{1}{2}}\;2_{2\frac{1}{2}}$	$1/5\,.\,a_{6s} + 1/5\,.\,a_{6p}(\frac{1}{2}) + 3/5\,.\,a_{6p}(1\frac{1}{2})$	0·50	$a_{6p}(\frac{1}{2}) = 0{\cdot}66$ cm.$^{-1}$
$6s\,6p_{1\frac{1}{2}}\,6p_{1\frac{1}{2}}\;3_{2\frac{1}{2}}$	$1/5\,.\,a_{6s} + 4/5\,.\,a_{6p}(1\frac{1}{2})$	0·37	$a_{6p}(1\frac{1}{2}) = 0{\cdot}01$ cm.$^{-1}$
			A (calc.).
$6s\,6p_{\frac{1}{2}}\,6p_{\frac{1}{2}}\;4_{\frac{1}{2}}$	a_{6s}	2	1·80
$6s\,6p_{\frac{1}{2}}\,6p_{1\frac{1}{2}}\;5_{\frac{1}{2}}$	$-1/3\,.\,a_{6s} - 1/3\,.\,a_{6p}(\frac{1}{2}) + 5/3\,.\,a_{6p}(1\frac{1}{2})$	−0·8	−0·80
$6s\,6p_{\frac{1}{2}}\,6p_{1\frac{1}{2}}\;6_{1\frac{1}{2}}$	$-1/5\,.\,a_{6s} + 3/10\,.\,a_{6p}(\frac{1}{2}) + 9/10\,.\,a_{6p}(1\frac{1}{2})$	small	−0·15
$6s\,6p_{1\frac{1}{2}}\,6p_{1\frac{1}{2}}\;7_{1\frac{1}{2}}$	$-1/5\,.\,a_{6s} + 6/5\,.\,a_{6p}(1\frac{1}{2})$	−0·33	−0·35
$6s\,6p_{1\frac{1}{2}}\,6p_{1\frac{1}{2}}\;8_{\frac{1}{2}}$	a_{6s}	2	1·80

of the valence electrons given in the last column. Their values of these constants were used to obtain the values of A (calc.) for the other five terms of the configuration. As can be seen, the calculated and observed values agree well enough to justify our assignment of these terms to the $6s6p^2$ configuration. Fisher and Goudsmit's values of the interaction constants, given in the table, cannot be improved from our present measurements, since, as shown, each line used to evaluate the hyperfine structure intervals resolved only the structure of the term of the $6s6p^2$ configuration and not the structure of the other combining term.

An interesting feature of the hyperfine structure of Bi III is the comparatively large separations of the two $6d$ terms. Normally a $6d$ electron is expected to have a very small interaction with the magnetic nucleus. The unusually large structures observed are probably due to perturbation of the $6d$ terms by the overlapping $6s6p^2$ group. If this be so, the $6s6p^2$ and $6d$ terms should be considered together, and the summations carried out over the two configurations as a whole. As the $7s$ term also falls among the $6s6p^2$ group, it should, perhaps, be included in the summation. At present, however, the hyperfine structure separations of the $6d$ terms are not known with sufficient accuracy to warrant a summation over the three configurations. Since such hyperfine structure perturbations are now being considered from a theoretical point of view,* it is desirable to obtain as much accurate information as possible about the effect. Accordingly we are preparing to measure the hyperfine structure separations of these terms of Bi III with a new 21-foot concave grating, recently set up in this laboratory.

To complete the information on the hyperfine structure of Bi III it should be mentioned that Goudsmit (*loc. cit.*) has calculated the interaction constants

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* Goudsmit, 'Phys. Rev.,' vol. 43, p. 636 (1933) and Breit and Wells, communication to Professor J. C. McLennan; about to be published.

$a_{7p}(\frac{1}{2}) = 0\cdot102$ cm.$^{-1}$, $a_{7p}(1\frac{1}{2}) = 0\cdot021$ cm.$^{-1}$, and Fisher and Goudsmit (*loc. cit.*) the constant, $a_{7s} = 0\cdot472$ cm.$^{-1}$, from the intervals of $7p\,^2P_{\frac{1}{2}}{}^0$, $7p\,^2P_{1\frac{1}{2}}{}^0$, and $7s\,^2S_{\frac{1}{2}}$ respectively, which were measured by the latter investigators.

The results of the analysis of Bi II are given in Tables III and IV. The more stable terms of Bi II have a characteristic distribution in well-defined, isolated groups; while most of the higher terms exhibit no distinctive grouping. As the assignment of electron configurations has a significance and can

Table III.—Terms of Bi II.

Term.		Value cm.$^{-1}$.	Total hyperfine structure interval.§
$6p_{\frac{1}{2}}\ 6p_{\frac{1}{2}}$	1_0	0*	—
$6p_{\frac{1}{2}}\ 6p_{1\frac{1}{2}}$	2_1	13324	—
	3_2	17030	—
$6p_{1\frac{1}{2}}\ 6p_{1\frac{1}{2}}$	4_2	33936	—
	5_0	44173	—
$6p_{\frac{1}{2}}\ 7s$	$1_0{}^0$	69133	—
	$2_1{}^0$	69598	3·91
$6s\ 6p^3$	$4_2{}^0$	76147	8·2
$6p_{\frac{1}{2}}\ 6d_{1\frac{1}{2}}$	$5_2{}^0$	79089	2·55
	$6_1{}^0$	80575	−1·65
$6p_{\frac{1}{2}}\ 6d_{2\frac{1}{2}}$	$7_2{}^0$	82047	1·98
	$8_3{}^0$	82255	—
$6p_{\frac{1}{2}}\ 7p_{\frac{1}{2}}$	6_1	84281	2·68‖
	7_0	87078	—
$6p_{\frac{1}{2}}\ 7p_{1\frac{1}{2}}$	8_1	88566	−1·02
$6p_{1\frac{1}{2}}\ 7s$	$9_2{}^0$	88769	2·18
$6p_{\frac{1}{2}}\ 7p_{1\frac{1}{2}}$	9_2	88789	2·50
$6p_{1\frac{1}{2}}\ 7s$	$10_1{}^0$	89883	−0·53
$6s\ 6p^3$	$11_1{}^0$	94440	—
	$12_2{}^0$	94928	—
	$13_3{}^0$	96057	—
$6p_{1\frac{1}{2}}\ 6d$ $6p_{\frac{1}{2}}\ 8s$ $6s\ 6p^3$	$14_2{}^0$	99011	—
	$15_1{}^0$	100492	—
	$16_1{}^0$	101341	—
	$17_0{}^0$	101464‡	—
	$18_2{}^0$	102330	—
	$19_3{}^0$	103003	—
$6p_{\frac{1}{2}}\ 5f_{2\frac{1}{2}}$ and $6p_{1\frac{1}{2}}\ 7p$ or $6p_{\frac{1}{2}}\ 8p$	10_2	105083	−0·16
	11_2	105269	—
$6p_{\frac{1}{2}}\ 5f$	12_2	105287	−0·70
	13_3	105449	1·95
$6p_{\frac{1}{2}}\ 7d$ or $6s\ 6p^3$	$20_2{}^0$	105526	2·48‖
$6p_{\frac{1}{2}}\ 5f_{3\frac{1}{2}}$	14_4	105726	—
$6p_{1\frac{1}{2}}\ 7p$ or $6p_{\frac{1}{2}}\ 8p$	15_1	106447	−0·36
$6p_{\frac{1}{2}}\ 7d$ or $6s\ 6p^3$	$21_1{}^0$	106611	−0·85‖
$6p_{1\frac{1}{2}}\ 7p_{1\frac{1}{2}}$ or $6p_{\frac{1}{2}}\ 8p_{\frac{1}{2}}$	21_0	107976	—
$6p_{\frac{1}{2}}\ 7d$ or $6s\ 6p^3$	$22_3{}^0$	108007‡	—
$6p_{\frac{1}{2}}\ 7d$ or $6s\ 6p^3$	$23_1{}^\circ$	108126	—
$6p_{1\frac{1}{2}}\ 7p_{1\frac{1}{2}}$	16_3	108278	0·37
$6p_{1\frac{1}{2}}\ 7p$ $6p_{\frac{1}{2}}\ 8p$	17_1	108404	−0·14
	22_2	108886	—
	18_1	109104	—
$6p_{\frac{1}{2}}\ 7d$ or $6s\ 6p^3$	$24_2{}^0$	109157	—
$6p_{1\frac{1}{2}}\ 7p$ or $6p_{\frac{1}{2}}\ 8p$	19_2	109904	0·78
$6p_{\frac{1}{2}}\ 6f$	23_3	115933	—
	24_4	115990‡	—
	25_3	116089	—
	26_2	116212	—
$6p_{\frac{1}{2}}\ 5g$	25^0	117004†	—

§ See Fisher and Goudsmit, *loc. cit.*

* Value of this term relative to $6p\,^2P_{\frac{1}{2}}{}^0$ of Bi III is 134600 cm.$^{-1}$; (see †). Value relative to $6p\,^2P_{1\frac{1}{2}}{}^0$ of Bi III is then 155388, as the $^2P^0$ interval is equal to 20788 (see Table I).

† Assumed hydrogenic for the calculation of limits in *.

‡ Not as well established as other terms.

‖ Intervals measured by Fisher and Goudsmit in the patterns of previously unclassified lines (see Table IV, reference ¶).

Two terms designed 8^0 and 20_0 given in our previous term table have been found unreal and are omitted here.

Table IV.—Classification Wave-lengths of Bi II.

Intensity.		λ (I.A.).	ν.	Classification.
Arvidsson.	Crawford and McLay.			
—	25	8863	11280	14_4—25^0
—	8*b*	8682	11515	12_2^0—15_1
—	25	53	11554	13_3—25^0
—	30	8532	11717	12_3—25^0
—	15	8388	11919	10_2—25^0
—	15	28	12005	11_1^0—15_1
—	8*b*	8183	12217	13_3^0—16_3
—	12*b*	8050	12419	4_2^0—8_1
—	20	7965	12552	9_2—16_1^0
—	5*b*	08	12642	4_2^0—9_2
—	5	7825	12776	8_1—16_1^0
—	10	7750	12900	8_1—17_0^0
—	10*b*	7637*	13090	19_3^0—25_3
—	5*b*	7388	13534	11_1^0—21_0
—	10*b*	81*	13545	9_2—18_2^0
—	2	7262	13767	8_1—18_2^0
—	12	7033	14215	9_2—19_3^0
—	3	10	14262	7_0—16_1^0
—	50B	6808·6	14683	2_1^0—6_1
—	40B	6600·2	15147	1_0^0—6_1
—	10	6577·2	15200	10_1^0—10_2
—	15	6497·7	15386	10_1^0—11_2
—	15	6128·0	16314	9_2^0—10_2
—	15	6059·1	16500	9_2^0—11_2
—	5	52·3	16518	9_2^0—12_2
—	8	35·6	16564	10_1^0—15_1
—	20	5973·0	16737	9_2—20_2^0
—	3	5894·6	16960	8_1—20_2^0
—	20	5860·2	17060	6_1—16_1^0
—	5	53·9	17078	14_2^0—25_3
—	12	18·3	17182	6_1—17_0^0
—	4	12·3	17200	14_2^0—26_2
—	40B	5719·2‖	17480	2_1^0—7_0
—	20	5655·2	17678	9_2^0—15_1
—	8	5540·2	18045	8_1—21_1^0
—	2	25·5	18093	10_1^0—21_0
—	10	5397·8	18521	10_1^0—17_1
—	40B	5270·3‖	18969	2_1^0—8_1
—	8	60·8	19003	10_1^0—22_2
—	75B	09·2	19191	2_1^0—9_2
—	20	01·5	19220	10_1^0—18_1 and 9_2—22_3^0
—	7	5169·9	19337	9_2—23_1^0
—	60*b*	44·3‖	19434	1_0^0—8_1
—	50*b*	24·3‖	19509	9_2^0—16_3
—	8	18·2	19533	7_0—21_1^0
—	5	11·0	19560	8_1—23_1^0
—	10	5091·6‖	19635	9_2^0—17_1
—	5	29·5	19877	13_3^0—23_3
—	20	4993·6‖	20020	10_1^0—19_2
—	12	69·7	20116	9_2^0—22_2
—	10	16·6	20334	9_2^0—18_1

b Broad.

B *Very broad; hyperfine structure partially resolved but difficult to measure.*

* Also classified in Bi III—see Table II.

‖ Hyperfine structure measured by Fisher and Goudsmit, *loc. cit.*

Table IV—(continued).

Intensity.		λ (I.A.).	ν.	Classification.
Arvidsson.	Crawford and McLay.			
—	12	08·2	20368	$9_2 — 24_2^{\circ}$
—	2	4759·7	21004	$12_2^{\circ} — 23_2$
—	20	49·7	21048	$7_0 — 23_1^{\circ}$
—	30	30·3‖	21134	$9_2^{\circ} — 19_2$
—	60B	05·3‖¶	21246	$6_1 — 20_2^{\circ}$
—	7	4696·3	21287	$12_2^{\circ} — 26_2$
—	25B	4476·8‖¶	22331	$6_1 — 21_1^{\circ}$
—	12*b*	4379·4	22828	$8_3^{\circ} — 10_2$
—	2	44·5	23011	$8_3^{\circ} — 11_2$
—	25*b*	40·5‡	23032	$8_3^{\circ} — 12_2$
—	12*b*	39·8	23036	$7_2^{\circ} — 10_2$
—	8	10·3	23194	$8_3^{\circ} — 13_3$
—	5	05·4*	23220	$7_2^{\circ} — 11_2$
—	70*b*	01·7‖	23240	$7_2^{\circ} — 12_2$
—	25	4272·0	23402	$7_2^{\circ} — 13_3$
—	75*b*	59·4	23471	$8_3^{\circ} — 14_4$
—	8	4192·56	23845·1	$6_1 — 23_1^{\circ}$
—	6	92·31	23846·5	
—	4	92·10	23847·7	
—	10	4097·2	24400	$7_2^{\circ} — 15_1$
—	40*b*	79·1‖	24508	$6_1^{\circ} — 10_2$
—	2	48·4	24694	$6_1^{\circ} — 11_2$
—	3*b*	18·6	24877	$6_1 — 24_2^{\circ}$
—	3*b*	3931·9	25426	$5_0 — 2_1^{\circ}$
—	30	3863·9‖	25873	$6_1^{\circ} — 15_1$
—	10	45·8‖	25995	$5_2^{\circ} — 10_2$
—	5	41·6	26023	$8_3^{\circ} — 16_2$
—	3	18·6	26180	$5_2^{\circ} — 11_2$
—	20	15·8‖	26199	$5_2^{\circ} — 12_2$
—	12	11·1‖	26232	$7_2^{\circ} — 16_2$
—	2	3797·0	26329	$10_1^{\circ} — 26_2$
—	5	93·0†	26357	$7_2^{\circ} — 17_1$
—	70*b*	92·5‖	26360	$5_2^{\circ} — 13_3$
—	4	54·0	26631	$8_3^{\circ} — 22_2$
—	8	3724·9‡	26839	$7_2^{\circ} — 22_2$
—	5	3659·4	27319	$9_2^{\circ} — 25_2$
—	12	54·2	27358	$5_2^{\circ} — 15_1$
—	5	48·3	27402	$6_1^{\circ} — 21_0$
—	2	15·8	27649	$8_3^{\circ} — 19_2$
—	2	3592·4	27829	$6_1^{\circ} — 17_1$
—	8	88·5	27859	$7_2^{\circ} — 19_2$
—	4	04·2	28529	$6_1^{\circ} — 18_1$
—	5	3455·28	28933·0	$4_2^{\circ} — 10_2$
—	3	55·01	28935·2	
—	2	54·82	28936·8	
—	2*b*	54·5	28939	

b Broad.

B Very broad; hyperfine structure partially resolved but difficult to measure.

* Also classified in Bi III—see Table II.

† Possibly a diffraction edge of 3792·5.

‡ Merged with Bi IV line.

‖ Hyperfine structure measured by Fisher and Goudsmit, *loc. cit.*

¶ Fisher and Goudsmit interpreted the hyperfine structure patterns of these lines which at that time were unclassified. The line 4476·8, which is completely resolved with only the faint centre component missing, was interpreted by them as a J = 2 to J = 2 transition. The pattern, however, fits exactly a J = 1 to J = 1 transition as given in the table above.

Table IV—(continued).

Intensity.		λ (I.A.).	ν.	Classification.
Arvidsson.	Crawford and McLay.			
—	12	31·23‖	29135·7	4_2^0—12_3
—	10	30·83	29139·1	
—	8	30·53	291141·7	
—	6	30·30	29143·6	
—	4	30·10	29145·3	
—	4B	11·8	29302	4_2^0—13_3
—	2	10·1	29316	5_2^0—17_1
—	4	08·6	29329	6_1^0—19_2
—	6	3355·1	29797	5_2^0—22_2
—	3	30·5	30017	5_2^0—18_1
—	4	3299·79 ‡	30296·3	4_2^0—15_1
—	3	99·57	30298·3	
—	3B	99·3	30301	
—	5	3111·67	32127·8	4_2^0—16_3
—	4	11·41	32130·5	
—	3	11·20	32132·6	
—	2	11·02	32134·5	
—	1	10·88	32136·0	
—	7B	3053·7	32737	4_2^0—22_2
—	8B	33·5	32956	4_2^0—18_1
—	7	2968·3	33679	8_3^0—23_3
—	12	63·4	33735	8_3^0—24_4
—	6	54·7	33834	8_3^0—25_3
—	20	50·4	33884	7_2^0—23_3
—	15	2936·7‡	34042	7_2^0—25_3
—	5	26·1	34165	7_2^0—26_2
—	5	2817·36	35483·8	2_1^0—10_2
—	2	17·17	35486·2	
—	3	17·01	35488·2	
—	12	05·3	35636	6_1^0—26_2
—	11	03·70	35656·7	4_2 — 2_1^0
—	9	03·58	35658·2	
—	15	03·42	35660·2	
—	2	02·70	35669·4	2_1^0—11_2
—	2	02·55	35671·3	
—	1	02·44	35672·7	
—	5	2746·36	36401·1	5_0 — 6_1^0
—	4*b*	46·2	36403	
—	20	13·3§	36844	5_2^0—23_2
—	5	01·8	37001	5_2^0—25_3
—	12	2693·0‡	37122	5_2^0—26_2
—	4	79·2	37314	1_0^0—15_1
—	2	04·95	38377	2_1^0—21_0
—	2	04·82	38379·0	
—	1	04·63	38381·8	
—	5	2545·6	39272	1_0^0—17_1
—	20B	44·5	39289	2_1^0—22_2
—	4	30·56	39505·1	2_1^0—18_1
—	3	30·41	39507·4	
—	3	30·28	39509·4	

b Broad.

B Very broad; hyperfine structure partially resolved but difficult to measure.

‡ Merged with Bi IV line.

§ Superimposed on very broad, unresolved, unclassified, faint hyperfine structure pattern. The predicted line $2_1^0 - 15_1$ ($\nu = 36849$) is probably obscured by the same pattern.

‖ Hyperfine structure measured by Fisher and Goudsmit, *loc. cit.*

Table IV—(continued).

Intensity.		λ (I.A.).	ν.	Classification.
Arvidsson.	Crawford and McLay.			
—	8B	12·6	39787	$4_2^0-23_3$
—	4	03·12	39938·1	$4_2^0-25_3$
—	3	02·92	39941·3	
—	2	02·76	39943·9	
—	2	02·63	39945·9	
—	1	02·53	39947·5	
—	10	01·0	39972	$1_0^0-18_1$
—	2	2495·3	40063	$4_2^0-26_2$
—	—	——‡	——	
—	2*b*	95	40069	
—	3	80·25	40306·3	$2_1^0-19_2$
—	2	80·12	40308·5	
—	2	80·03	40309·9	
—	8	2368·54	42207·2	$4_2-4_2^0$
—	9	68·46	42208·6	
—	10	68·37	42210·2	
—	12	68·25	42212·3	
—	16	68·12	42214·7	
—	40*b*	2214·0	45153	$4_2-5_2^0$
—	60	2186·9	45712	$5_0-10_1^0$
—	15	43·46	46638·8	$4_2-6_1^0$
—	15	43·40	46640·1	
—	10	43·35	46641·2	
—	8	2077·8	48112	$4_2-7_2^0$
—	45*b*	68·9*	48319	$4_2-8_2^0$
		λ (I. vac.).		
—	25	1989·35	50268	$5_0-11_1^0$
—	100*b*	02·41	52565	$3_2-2_1^0$
—	70	1823·80	54831	$4_2-9_2^0$
—	70	1791·93	55806	$2_1-1_0^0$
—	60	87·47	55945	$4_2-10_1^0$
—	80	77·11	56271	$2_1-2_1^0$
—	10	75·56	56320	$5_0-15_1^0$
—	20	49·29	57166	$5_0-16_1^0$
—	20*b*	1691·5*	59120	$3_2-4_2^0$
—	20	52·81	60503	$4_2-11_1^0$
—	40	11·38	62059	$3_2-5_2^0$
—	40	09·70	62122	$4_2-13_3^0$
—	25	01·58	62438	$5_0-21_1^0$
—	60B	1591·79	62822	$2_1-4_2^0$
—	40	73·70	63545	$3_2-6_1^0$
—	20	63·67	63952	$5_0-23_1^0$
—	35	38·06	65017	$3_2-7_2^0$
—	30	36·77	65071	$4_2-14_2^0$
—	40	1533·17	65224	$3_2-8_2^0$
—	40	20·57	65765	$2_1-5_2^0$
—	20	02·50	66556	$4_2-15_1^0$
6	35	1486·93	67253	$2_1-6_1^0$
6	25	62·14	68393	$4_2-18_2^0$
25	50	55·11	68723	$2_1-7_2^0$

b Broad.
B Very broad; hyperfine structure partially resolved but difficult to measure.
* Also classified in Bi III—see Table II.
‡ Merged with Bi IV line.

Table IV—(continued).

Intensity.		λ (I. vac.).	ν.	Classification.
Arvidsson.	Crawford and McLay.			
3	25	47·94	69064	$4_2 - 19_3^0$
20	45	36·83	69598	$1_0 - 2_1^0$
—	5	1396·91	71587	$4_2 - 20_2^0$
6	20	93·92	71740	$3_2 - 9_2^0$
1	15	76·02	72673	$4_2 - 21_1^0$
8	25	72·61	72854	$3_2 - 10_1^0$
5	20	50·07	74070	$4_2 - 22_3^0$
—	8	47·94	74187	$4_2 - 23_1^0$
8	20	29·47	75218	$4_2 - 24_2^0$
5	20	25·46	75445	$2_1 - 9_2^0$
6	10	06·18	76559	$2_1 - 10_1^0$
—	5	1291·83	77409	$3_2 - 11_1^0$
6	15	83·73	77898	$3_2 - 12_2^0$
—	10	65·35	79029	$3_2 - 13_3^0$
10	10	41·05	80577	$1_0 - 6_1^0$
2	15	32·78	81117	$2_1 - 11_1^0$
6	10	25·43	81604	$2_1 - 12_2^0$
—	5	19·80	81981	$3_2 - 14_2^0$
3	5	1198·15	83462	$3_2 - 15_1^0$
—	3	86·06	84313	$3_2 - 16_1^0$
2	5	72·33	85300	$3_2 - 18_2^0$
9	8	67·06	85685	$2_1 - 14_2^0$
9	8	1163·19	85970	$3_2 - 19_3^0$
4	5	47·19	87169	$2_1 - 15_1^0$
3	3	23·54	89004	$2_1 - 18_2^0$
1	3	12·54	89884	$1_0 - 10_1^0$
8	10	1099·20	90975	$3_2 - 22_3^0$
1	5	97·76	91095	$3_2 - 23_1^0$
7 (?)	20	85·47	92126	$3_2 - 24_2^0$
7	15	58·88	94439	$1_0 - 11_1^0$
1	—	937·95	106616	$1_0 - 21_1^0$

be carried out with certainty only when the states arising from different configurations do not intermix too much, only the terms in isolated groups have been allotted unique configuration classifications. The distribution of these terms shows that the coupling in the two-electron spectrum approximates to the extreme (*jj*) type. Configurations could not be assigned uniquely to the majority of the higher terms on account of the intermingling of the terms from the less stable configurations with resulting perturbations. Some information about the electronic origins of these terms, however, was ascertainable. By using the values of the two ionization potentials (see footnote, Table III) and the data obtainable from the identifiable deeper terms, it was possible to predict approximately the position of the higher terms arising from the various less stable electron configurations. Using this information, and the J values of the terms as found from their combining properties, it was possible to specify for a number of the higher terms the origin of each as being in one or other of two overlapping configurations; and to give for each of the remaining groups of terms the two or more configurations contributing to the group.

A few of the more stable terms of the lowest four-electron configuration $6s6p^3$ have been definitely identified. From their distribution it appears that the coupling of the four electrons is of an intermediate type similar to that of the three-electron configuration $6s6p^2$ of Bi III. Higher terms of the $6s6p^3$ configuration are probably among the established levels, but cannot be uniquely identified since they intermix with the higher two-electron terms.

Two terms of Bi II reported in our previous communication have been found to be spurious. One, designated 3^0, had been shown to be unreal by Fisher and Goudsmit (*loc. cit.*) from their hyperfine structure measurements. The other, designated 20_0, has been discarded by us for two reasons: first, the hyperfine structure of the line $\nu = 41334$, previously classified as $2_1{}^0-20_0$ and used to establish 20_0, has been found to be inconsistent with the hyperfine structure of the $2_1{}^0$ term as determined from other well-established transitions; and second, the line $\nu = 21048$, which was identified in our previous analysis as $10_1{}^0-20_0$ and was the only other combination establishing 20_0, has been more satisfactorily classified in this investigation.

The hyperfine structure of Bi II has been discussed by Fisher and Goudsmit (*loc. cit.*). The hyperfine structure intervals measured by them are listed opposite their respective terms in Table III. Although the three terms 6_1, $20_2{}^0$, and $21_1{}^0$ were not established previous to this investigation, their hyperfine structure intervals were available through Fisher and Goudsmit's measurements of the structures of the then unclassified lines 4705 A. and 4477 A. These lines have been classified in this analysis as the transitions $6_1-20_2{}^0$ and $6_1-21_1{}^0$ respectively. Thus the intervals derived from their structures by Fisher and Goudsmit are the intervals of the terms 6_1, $20_2{}^0$, and $21_1{}^0$. As two possibilities arise in the interpretation of the structure of an unclassified line since there is no way of deciding which level is initial, Fisher and Goudsmit could only give the interval of each of the terms involved as one or other of two alternative values. The classification of the two lines has removed this ambiguity and made it possible to select uniquely the intervals of the three terms. Our assignment of the value $J = 1$ to the initial and final levels of the line 4477 A. differs from Fisher and Goudsmit's. They indicate in their table that the initial and final levels both have $J = 2$. The line, however, is well established by our analysis as the combination $6_1-21_1{}^0$;

moreover, its structure fits exactly a $J = 1$ to $J = 1$ transition. In all probability the J values given in their table are misprints.

The term 6_1 belongs to the isolated group $6p_{\frac{1}{2}}7p$; and since the hyperfine intervals of all terms of this group are now known fairly accurately, good values of the interaction constants of the two p electrons can be deduced, provided the coupling is as near (jj) as supposed. The calculations are given in the following table.

Term.	A, (jj) coupling.	A (obs.).
		cm.$^{-1}$
$6p_{\frac{1}{2}}$ $7p_{\frac{1}{2}}$ 6_1	(1) $\frac{1}{2}a_{6p}(\frac{1}{2}) + \frac{1}{2}a_{7p}(\frac{1}{2})$	$0\cdot268$
$6p_{\frac{1}{2}}$ $7p_{1\frac{1}{2}}$ 8_1	(2) $-\frac{1}{4}a_{6p}(\frac{1}{2}) + 1\frac{1}{4}a_{7p}(1\frac{1}{2})$	$-0\cdot102$
$6p_{\frac{1}{2}}$ $7p_{1\frac{1}{2}}$ 9_2	(3) $\frac{1}{4}a_{6p}(\frac{1}{2}) + \frac{3}{4}a_{7p}(1\frac{1}{2})$	$0\cdot125$
From (2) and (3)	$a_{6p}(\frac{1}{2}) = 0\cdot465$; Substituting $a_{6p}(\frac{1}{2})$ in (1), $a_{7p}(\frac{1}{2}) = 0\cdot070$.	$a_{7p}(1\frac{1}{2}) = 0\cdot012$

The values of $a_{6p}(\frac{1}{2})$ and $a_{7p}(1\frac{1}{2})$ were given by Fisher and Goudsmit, but that of $a_{7p}(\frac{1}{2})$ is new. The above results lead to the value 6/1 for the ratio $a_{7p}(\frac{1}{2})/a_{7p}(1\frac{1}{2})$. This is in fair agreement with the ratio 5/1 determined by Goudsmit (*loc. cit.*) from the hyperfine separations of the $7p$ terms of Bi III. Thus the ratio $a_{7p}(\frac{1}{2})/a_{7p}(1\frac{1}{2})$ as determined from both Bi II and Bi III is close to the theoretical ratio 5/1 predicted for a not too penetrating p electron.

By using the above value of $a_{7p}(1\frac{1}{2})$ the interaction constant $a_{6p}(1\frac{1}{2})$ can be evaluated from the interval of the term 16_3 ($6p_{1\frac{1}{2}}\,7p_{1\frac{1}{2}}$). As this term is independent of coupling, the formula $A(16_3) = \frac{1}{2}a_{6p}(1\frac{1}{2}) + \frac{1}{2}a_{7p}(1\frac{1}{2})$ is applicable. The substitution of the values $A(16_3) = 0\cdot012$ and $a_{7p}(1\frac{1}{2}) = 0\cdot012$ in this formula gives $a_{6p}(1\frac{1}{2}) = 0\cdot012$. This is in fair agreement with the values $0\cdot01$ and $0\cdot028$ deduced by Fisher and Goudsmit from Bi III and Bi II terms respectively.

Fisher and Goudsmit have also calculated the following constants: $a_{6s} = 1\cdot60$ from $4_2{}^0$ of the $6s6p^3$ configuration; $a_{6p}(\frac{1}{2}) = 0\cdot430$, $a_{6p}(1\frac{1}{2}) = 0\cdot028$ and $a_{7s} = 0\cdot352$ from $2_1{}^0$, $9_2{}^0$, and $10_1{}^0$ of the $6p7s$ configuration; and the very uncertain ones $a_{6p}(\frac{1}{2}) = 0\cdot565$, $a_{6d}(1\frac{1}{2}) = -0\cdot019$ from $5_2{}^0$ and $6_1{}^0$ of the $6p_{\frac{1}{2}}\,6d_{1\frac{1}{2}}$ configuration.

They questioned our assignment of the term $7_2{}^0$ to the configuration $6p_{\frac{1}{2}}\,6d_{2\frac{1}{2}}$, because its hyperfine structure is inconsistent with the theoretical formula. We believe, however, that the terms of the $6p_{\frac{1}{2}}6d$ configuration are correctly identified in Table III of both this and our previous paper, and that the discrepancies between the observed hyperfine structures of the $6p_{\frac{1}{2}}6d$ terms and the theoretical formulæ are due to the perturbation of the two terms with $J = 2$ by the adjacent 4_2^0 term.

Fisher and Goudsmit found that the hyperfine structure separations of the terms 10_2, 12_3, 13_3, of the $6p_{\frac{1}{2}}5f$ configuration were not consistent with the (jj) coupling formulæ for the interval factors of these terms. As the coupling of the f electron is not strictly (jj) only the sum relations can be justly applied to this configuration. The expression for the sum of the interval factors of 12_3 and 13_3 is $A(12_3) + A(13_3) = 1/24 \, . \, a_{6p}(\frac{1}{2})$ when the $5f$ interactions, which are expected to be small, are neglected. The experimental value of $A(12_3) + A(13_3) = 0{\cdot}042$ when substituted in this equation gives $a_{6p}(\frac{1}{2}) = 1{\cdot}00$. The minimum value of $A(12_3) + A(13_3) = 0{\cdot}030$, corresponding to the maximum error given by Fisher and Goudsmit, gives $a_{6p}(\frac{1}{2}) = 0{\cdot}72$. These values are of the right order of magnitude, although somewhat larger than the values of $a_{6p}(\frac{1}{2})$ found from other terms. The inclusion of the $5f$ interactions would tend to reduce the above values; but as the magnitude of the $5f$ interaction constants cannot be determined from the data available, one cannot say whether or not the reduction would be sufficient to give good agreement. The determination of the interval factor of the term $6p_{\frac{1}{2}}5f_{3\frac{1}{2}}$ 14_4, which is independent of coupling, would give sufficient information to settle the point. From the above considerations it appears that the discrepancy between the measured and the calculated interval factors of 12_3 and 13_3 is not great enough to invalidate our assignment of them to the $6p_{\frac{1}{2}}5f$ configuration, especially as this assignment is well supported by the term analyses. It is possible but not probable that 12_3 and 13_3 are appreciably perturbed by other terms of the same parity: 16_3, which is about 3000 cm.$^{-1}$ from 12_3 and 13_3, is the only identified term that might be expected to perturb them, and its effect certainly is small since the magnitude of its interval factor, $A(16_3)$, is in good agreement with the value predicted for 16_3 as unperturbed; further, no prominent unidentified even terms with $J = 3$ are expected near enough to 12_3 and 13_3 appreciably to perturb them.

The interval factor of 10_2, which according to our previous classification as $6p_{\frac{1}{2}}5f_{2\frac{1}{2}}$ is independent of coupling, does not agree at all with the value predicted by the appropriate formula. This discrepancy is undoubtedly due to the mutual perturbation of 10_2 and the adjacent 1^1_2 term, as suggested by Fisher and Goudsmit. Since these two terms through perturbation share their characteristics, it is not justifiable to assign a specific configuration to either; they should be considered together. Accordingly they have been grouped in this classification. The mutual perturbation of these two terms is also evident in their combining characteristics. The combinations of 10_2 with the $6p7s$ terms show that it has some of the characteristics of a $6p, p$ term. If 10_2 were strictly a $6p_{\frac{1}{2}}5f$ term these combinations, although permitted by the Laporte rule, would not be expected since they would require the azimuthal quantum number of the jumping electron to change by three instead of one as usually observed for single-electron transitions. The predominance of the intensities of the combinations of 1^1_2 with the $6s7p$ terms over the intensities of the combinations of 10_2 with the same terms, and the presence of the combination 10_2—25° ($6p_{\frac{1}{2}}5g$) contrasted with the absence of 11_2—25°, indicate that the $6p, p$ characteristics predominate in 11_2 and the $6p5f$ characteristics in 10_2.

In conclusion we wish to thank Professor E. F. Burton, Director of the McLennan Laboratory, for his interest in this investigation and for the facilities placed at our disposal.

Summary.

This paper gives the results of an extended investigation of the term structures of the spectra of Bi II and Bi III. The values of these spectral terms are recorded and tables of classified wave-lengths between 10,000 A. and 175 A. that were used in evaluating them are given in the paper. The paper includes considerable information on the fine structure of the spectral lines analysed.

The Dielectric Coefficients of Gases.—Part II. *The Lower Hydrides of Carbon and Silicon, Oxygen, Nitrogen, Oxides of Nitrogen and Carbon, and Fluorides of Silicon and Sulphur.*

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(Communicated by Sir Martin Forster, F.R.S.—Received September 12, 1933.)

In Part I* measurements of the dielectric coefficients of hydrogen and the rare gases at two temperatures were recorded. The investigation has now been extended to a number of other gases with a view to determining the electric moment of their molecules and comparing the values of the dielectric coefficient with those of the refractive index at long wave-lengths. The results now given are those of a series of measurements dating from 1928, and during their progress several papers comprising the same subject have been published. These will be discussed later and the results compared.

When dealing with all but the simplest gases a knowledge of the compressibility is essential in order to reduce the values of the dielectric coefficient at different temperatures to those for equal density; it is also desirable to employ gases which have been purified with the greatest care. The compressibilities of the gases under reference have been determined approximately by measuring the dielectric coefficients at different pressures as for ammonia† and several values have been confirmed by direct determination or by refractometric measurements, an account of which will be given elsewhere.

Determinations have been made by the "series" method previously employed and also by the "parallel" method using a condenser specially constructed for measuring very small capacity changes. The results given by the two methods are in satisfactory agreement. The following gases have been examined: methane, ethane, propane, ethylene, propylene, acetylene, silicane, silicoethane, carbon monoxide and dioxide, oxygen, nitrogen, air, nitrous oxide, nitric oxide, silicon tetrafluoride and sulphur hexafluoride. Of these only propylene, carbon monoxide and the two oxides of nitrogen have a measurable electric moment.

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* 'Proc. Roy. Soc.,' A, vol. 132, p. 569 (1931).

† Watson, 'Proc. Roy. Soc.,' A, vol. 117, p. 59 (1927).

Experimental.

Measurements were made by the resonance method at a frequency of 960 kc./sec. mainly with the apparatus described in Part I, auxiliary condensers and gas pressures being arranged so that a change of about 1000 scale divisions was registered on the variable condenser when the gas condenser was filled or emptied. In general, measurements were confined to one region of the scale, the total length of which was 4000 divisions. After a number of experiments had been performed, it was found that if the upper region of the scale was used, the results were nearly 2% higher, a difference which could not be accounted for by any calibration errors. By making a number of determinations of the dielectric coefficient of oxygen, subsequently confirmed with the help of the parallel condenser about to be described, the variation of the results with the mean scale reading was ascertained. It was found that in the region normally used (500–1800 divisions) the deviation from the mean did not exceed 0·7% and thus only a small correction for lack of uniformity was necessary. This was applied in calculating the results, but the absolute value still remained uncertain. The exact source of error could not be discovered, but it appeared to be due partly to the hole in the condenser casing about 2·5 cm. in diameter through which the insulated lead entered. Improving the screening by reducing the size of the hole had a slight effect, but did not eliminate the irregularity entirely. As it was not possible to earth the variable condenser as well as the gas condenser, a slight lack of rigidity in the former may have been a factor. In the absence of any definite evidence, the mean value of the results towards the lower end of the scale was taken as being correct.

It has been pointed out in previous communications that the use of Zahn's* series method is attended by certain disadvantages. The additional source of error now recorded makes it evident that the method is unsuitable for determining absolute values of the dielectric coefficient unless confirmed by independent measurements. It was therefore decided to make use of a very small variable condenser in parallel with the gas condenser. A precision condenser of step type originally described by Wolf† was constructed, details being shown in fig. 1. For some of the features we are indebted to the General Electric Company, who kindly allowed us to inspect a similar condenser at their Wembley research laboratories. The gunmetal screw had a pitch of

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* 'Phys. Rev.,' vol. 24, p. 400 (1924).

† 'Phys. Z.,' vol. 26, p. 353 (1925).

1 mm. and was ground true with a split brass nut. The nut actually used was of white metal machined to nearly the correct size and finished with a tap cut from a portion of the screw. The stepped rod was turned in a precision lathe and lapped true to 0·003 mm., the diameters of the two sections being 18·6 and 11·4 mm.; a key way cut at one end prevented rotation. The insulated electrode consisted of a brass tube 100 mm. long and 48·5 mm. in diameter turned true on the inside and silvered. It was held in position by 6 quartz rods set in tubes soldered to the outer casing and adjusted by screws. The lead was fixed in the centre of a quartz plate. The bearings of the central rod formed screens so that the capacity depended solely on the position of the step. One drum divided into 100 divisions was attached close to the condenser and another at the end of an extension handle, a worm gear being provided to count the turns. Backlash was small, but to eliminate it readings were always taken in the same direction. The total capacity of the condenser was 23 μμF and the change in capacity per centimetre 0·2 μμF.

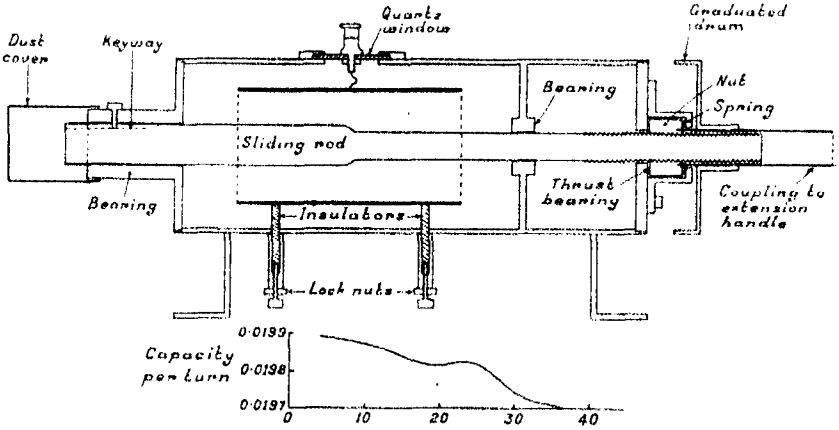

Fig. 1.

When using the heterodyne method the greatest accuracy with which it was possible to set the condenser was 0·5 scale division or 0·005 mm. and hence screw errors of this magnitude had little effect. The movement of the rod was measured with a comparator, and the maximum deviation from linearity, measured every whole millimetre, found to be 0·004 mm. There was in addition a periodic variation in certain portions of the screw amounting to most to 0·004 mm. These measurements showed that a high degree of uniformity was assured, but as a check and in order to determine the end effects which could not be calculated readily, the condenser was submitted to a step by step calibration.

For this purpose the condenser was connected as shown in fig. 2, *a*, the circuit drawn being the grid circuit of a valve oscillator turned to give 700 cycle beats with the first harmonic of a 960 kc./sec. crystal oscillator.

P represents the screw condenser, K the calibrated variable condenser, C a very small variable condenser and D and G fixed condensers of such magnitude (5000 and 140 μμF.) that the change in frequency produced by one revolution of the screw required K to be varied by 330 scale divisions to restore it to the original value. P was varied in steps of two revolutions and the corresponding change in K noted. By adjusting C, the initial reading of K could be brought to the same value for each measurement so that calibration and other errors were avoided. After applying small corrections for the change in relative magnitude of the series condensers, the calibration curve shown in fig. 1 was obtained, the result being the mean of several sets of concordant values taken on different occasions. By reversing this procedure, *i.e.*, by measuring the change in P necessary to compensate a change of, say, 400 divisions of K at different parts of the scale, the effective value of K at different settings was determined, the results, as already mentioned, differing very appreciably from the figures obtained by the ordinary calibration.

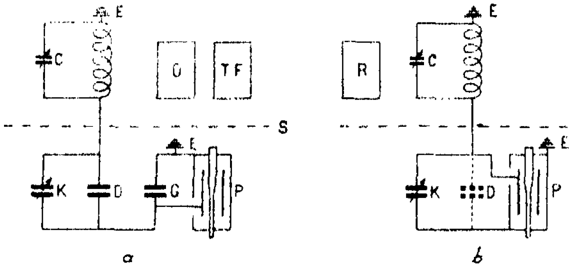

Fig. 2.

The value of P in terms of the standard quartz condenser Q was obtained by means of the circuit shown in fig. 2, *b*. P and K were connected in parallel in the grid circuit of the oscillator previously referred to and the whole tuned to resonance with the first harmonic of a 480 kc./sec. crystal oscillator Q, the receiver R making the beat note between the two system audible. The condenser D of suitable magnitude was then inserted and K varied until the circuit was tuned to the fundamental of the oscillator. The total capacity was then four times the original, or D plus the change in K was three times the capacity of the first circuit. D was measured in terms of Q by the methods described in I, giving the value of the capacity of the circuit when tuned to 480 kc./sec. This assumes the correctness of the LC rule which is known to be inaccurate for several valve oscillator circuits. In the present case, large alterations in the filament and grid currents, the usual source of variation, were found to change the apparent capacity by less than 1 part in 3000 so that it appeared legitimate to assume that the rule held good. The result was confirmed on several occasions by tuning the system to the third harmonic of the crystal, when it was found that the calculated value of the stray capacity agreed with that previously obtained, and the values deduced for the total capacity of the circuit did not differ by more than 1 part in 500.

After determining the capacity of the circuit, P was decreased until beats of about 434 cycles per second were obtained and then increased until the same frequency difference was reached, the frequency being measured by comparison with a tuning fork which was made to drive a phonic wheel throughout the experiment. The fork frequency varied from 433·9 to 434·2 according to temperature. The crystal frequency was determined by means of an intermediate 95·98 kc./sec. crystal oscillator. This frequency was measured by means of a step up multivibrator of the type described by Hull and Clapp* and the phonic wheel, measurements of several frequencies from 900 to 1200, all of which were submultiples of the crystal frequency being made. The 5th harmonic of this crystal had very nearly the same frequency as the 479·9 kc./sec. oscillator, no beats being audible. We are much obliged to Mr. S. K. Kulkarni Jatkar for making these determinations.

Knowing the absolute frequency and the capacity of the circuit, it should be possible to calculate the change in capacity for a difference of 868 cycles per sec., giving, after applying calibration corrections for uniformity, the capacity change in P per cm. Unfortunately the method, although simple in theory, was liable to be inaccurate in practice owing to the alteration in the frequency of the oscillating circuit produced when the receiver R was tuned to resonance. R, which had an aerial 7 feet long, was situated 9 feet from the former circuit, but the coupling was not sufficiently loose to eliminate frequency changes of a few parts in a million as R was tuned through resonance, and this was enough to produce a comparatively large error in the final result. The effect could be readily detected by taking readings for the octave as well as the fundamental of the tuning fork, when discordant and unsymmetrical results were obtained. For example, the following condenser settings were found for +434, +217, −217, and −434 cycles from resonance, the tuning of R being unaltered.

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* 'Proc. Inst. Radio Eng.,' vol. 27, p. 252 (1929).

	(1) 1263		(2) 2484		(3) 4923		(4) 6154
Difference		1221		2 × 1220		1231	

The difference between (3) and (4) is much greater than between the other pairs and is too great to be due to errors of setting which are not more than 2 units.

The effect could be eliminated by using a very sensitive receiver placed at a long distance, but this would be attended by certain disadvantages. Consistent results were finally obtained by allowing the oscillator to oscillate more strongly than usual, by using large inductances and consequently capacities as small as was consistent with their accurate measurement, by *reducing the coupling and detuning the receiver to the limit of audibility.* Measurements were made at ± 868 cycles/sec. when possible, the fundamental readings being used as a check. Three harmonic frequencies were used and several different inductances. As a result of numerous measurements, the value 0·1983 μμF. per cm. for the middle 20 mm. was obtained and this is believed to be correct to 1 part in 500. The value 0·1982 was deduced by calculation from the dimensions of the cylinders which were measured to 1 part in 4000 corresponding with an accuracy of at least ± 0·00015 μμF. The agreement is satisfactory.

The gas condenser G_3 used in some of the experiments described in I, although sufficiently rigid, had an unnecessarily small capacity and consequently another condenser G_4 was constructed, of similar design but larger, and with wider spacing between the plates. Three concentric gold plated brass tubes 1 mm. thick were used, the spacing being 0·80 mm. The total apparent capacity was 217 μμF. of which 0·25 μμF. was due to the quartz spacers, and 2·30 μμF. to the external leads. The lead inductance measured from P was 0·32 μH. A determination of the dielectric coefficient of pure benzene dried over phosphorus pentoxide for a week gave the value 2·267 at 28·8° agreeing with Hartshorn and Oliver's* value 2·2665. The compressibility of benzene measured as detailed in I was found to be $61 \cdot 2 \times 10^{-6}$ and the calculated value was $60 \cdot 3 \times 10^{-6}$ showing that the deformation of the condenser with pressure was very small. This was confirmed by measuring the dielectric coefficient of helium at room and liquid air temperatures. The results are shown in Table I.

* 'Proc. Roy. Soc.,' A, vol. 123, p. 664 (1929).

The refractive indices shown in the fourth column are for the mercury green line and are believed to be correct to 0·1 unit. They give an indication of the purity of the gas. Cuthbertson's* most recent value is 63·92 for the green line and 63·36 for very long wave-lengths. The figure obtained in experiment 25 in which the apparatus had not been rinsed with helium before introducing the gas indicates the presence of 0·11% of carbon dioxide, or 0·2% of water vapour as impurity. This amount of water would raise the dielectric coefficient by 17 units and hence the impurity must consist mainly of other gases. Carbon dioxide and water vapour would not affect the value at liquid air temperature. The gas used in the first four experiments had stood for 18 months and probably contained traces of air and water vapour which would give high values at both temperatures. These experiments indicate that the value of $(\epsilon - 1) \times 10^6$ measured at liquid air temperature is very near to 65 and at room temperature is about 63·5. If the difference were due to condenser deformation, the true value would be 65·5 at both temperatures coinciding with the value given in I for low temperatures. This, however, is 2 units higher than the value deduced from the refractive index, which appears improbable. Experiments at liquid air temperature are difficult to conduct and may be liable to a small constant error. It seems most likely therefore that distortion is negligible and that the true value is 64. This subject has been discussed at some length, as a measurement of the dielectric coefficient of helium is the easiest way of detecting pressure distortion in a condenser. The error in the value given is almost certainly not more than 1 unit and thus it is possible to detect any deformation greater than 1 part in a million.

Table I.—Dielectric Coefficient of Helium Calculated to 25°.

No.	Temperature.	$(\epsilon - 1) \times 10^6$.	$2(n - 1) \times 10^6$.	Remarks.
20	25·3	67·6	64·6	Gas purified 18 months earlier.
21	−191·5	*65·1*	—	—
22	−188·6	*65·2*	—	—
23	−190·2	*66·0*	—	—
24	26·2	63·5	64·15	After charcoal treatment.
25	23·0	66·6	64·8	Gas contaminated.
26	−191·4	*65·1*	—	,,
27	21·7	63·0	64·0	After charcoal treatment.
28	21·6	63·0	64·05	48 hours later.
29	−190·7	*64·2*	—	,,

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* 'Proc. Roy. Soc.,' A, vol. 135, p. 45 (1932).

When using the parallel condenser P it is necessary to apply a correction for its non-coincidence with G. If δG is the change in G on filling with gas, δP the amount by which P must be changed to restore the total capacity of the system to its original value and l the inductance of the leads from P to G, then

$$P + G + l\omega^2 G^2 = P - \delta P + G + \delta G + l\omega^2(G + \delta G)^2,$$

giving $\delta P = \delta G(l + 2l\omega^2 G)$ or $\delta G = \delta P(l - 2l\omega^2 G)$ since $l\omega^2 G$ is a small quantity. The actual value of this correction was 5·1 parts per 1000. The lead inductance correction when determining the capacity of the condenser was 2·5 parts per 1000 in the opposite sense so that the total inductance correction was only 2·6 parts per 1000 and an appreciable error in measuring the lead inductance would have very little influence on the final results.

Temperature Baths.

The same constant temperature baths as before were employed, viz., liquid air, solid carbon dioxide without a liquid medium, and oil at room temperature. For an intermediate temperature, phenetol at its melting point (—32°) was found convenient as it had less tendency to form hard lumps than chlorobenzene which was previously employed. It was, however, not entirely satisfactory as the temperature was not always quite uniform and rose by some 0·3° during the course of an afternoon. The value was determined at intervals with a thermocouple which in turn was compared with a mercury thermometer and checked at the melting point of mercury.

Preparation and Purification of Gases.

All the gases used were purified with great care, 0·1% being regarded as the maximum amount of impurity desirable, although it was not always possible to reach this limit. In the earlier experiments identity of the dielectric coefficients of the first and last fractions was taken as a criterion of sufficient purity; later, a Rayleigh refractometer kindly lent by Dr. B. Sanjiva Rao, of the Central College, Bangalore, was attached to the apparatus and afforded a more rapid and accurate method of examination. The refractive indices and dispersions of most of the gases have been measured and the results will form the subject of a later communication.

Methane was prepared by the action of zinc copper couple in an alcoholic solution of pure methyl iodide. In view of the known difficulty of separating methane from air, the apparatus, which was of as small a volume as possible, was initially filled with hydrogen. This gas was displaced before condensing the methane in liquid air. A middle fraction was taken and refractionated. No volume change could be observed on treating the gas with oxidized palladium sponge, indicating the absence of hydrogen. The weight of a litre of the gas measured at 27° and corrected to N.T.P. was 0·7194 gm. corresponding with a molecular weight of 16·006 and the vapour pressure at 86·3° K. was 44·5 mm.

Ethane was made in a similar manner to methane using ethyl iodide. A second preparation was made in an all glass apparatus which was evacuated after freezing the ethyl iodide in liquid air. On warming, the liquid was poured on to the couple and distillation to the rest of the apparatus prevented by a reflux condenser cooled with solid carbon dioxide.

In both preparations the gas after several fractionations contained ethylene. It was therefore liquefied in a tube containing bromine, allowed to rise to room temperature, again condensed and fractionated twice, first at —115° at which temperature its vapour pressure was 114 mm. and then from a bath of solidified ether-toluene mixture which reduced the vapour pressure to 50 mm. The difference in refractive index of the two fractions used in the experiments was not measurable.

Propane was made by reducing pure *iso*propyl iodide with zinc. The gas evolved was passed through concentrated potassium hydroxide solution, dried over solid potassium hydroxide and phosphorus pentoxide and condensed in liquid air. After two preliminary fractionations the gas was condensed in supercooled solid carbon dioxide and distilled. The vapour pressure varied only from 84 to 83 mm. and the gas appeared to be very pure. A portion of the gas was treated with bromine and compared in the refractometer with the original, the accuracy of the measurements being 1 part in 1000. No change could be observed.

Ethylene was prepared by the action of zinc on a 15% solution of pure ethylene dibromide in absolute alcohol with the addition of a trace of water. On condensation in liquid air the vapour pressure was constant at 30 mm. On refractionation, the vapour pressure and dielectric coefficient remained unchanged and the refractive indices of the first and last of seven fractions were identical to 1 part in 1000. In spite of this apparent high purity, 0·25% of the gas was not absorbed by bromine, the residue being a mixture of a hydrocarbon and air. The quantity of impurity was too small to alter the results appreciably.

Propylene obtained as a by-product in the catalytic dehydration of propyl alcohol was kindly supplied by Mr. N. G. Gajendragad. It was condensed in liquid air, small quantities of incondensable gas being pumped off, and then fractionated at the temperature of melting ether. The vapour pressure (—115°) was 6·5 mm. and the gas left a residue of only 0·21% after absorption by bromine. The weight of a normal litre measured at 27° was 1·9152 gm. corresponding with a molecular weight of 41·97 after correcting for compressibility (calc. C_3H_6, 42·05). The gas was subsequently fractionated several times and the three fractions used for the final measurements had the same refractive index to the limit of experimental error, the value of $(n - 1)^{25}_{5460}$ being 987·8.

Acetylene was prepared by the action of water on calcium carbide and purified by bubbling through solutions of copper sulphate, chromic acid, and potassium hydroxide. It was dried with solid potassium hydroxide and phosphorus pentoxide and condensed in liquid air. On distillation at —115° the vapour pressure varied from 38 to 34 mm., consequently the gas was again passed several times more through the purifying train, condensed and fractionated. On refractionation at —115° the initial vapour pressure was 35·5 mm., but after removing 8% of the gas the value fell to 34·5 mm. and remained constant. 99·9% of the gas was absorbed by bromine and the value of $(n-1)^{25}_{5460}$ was 551·7. The molecular weight calculated from density measurements with the microbalance was 26·01 agreeing with theory.

Silicomethane and silicoethane were made by dropping magnesium silicide into hydrochloric acid in an atmosphere of hydrogen and condensing the evolved gases in liquid air. After fractionation and removal of heavier constituents, the two lighter gases were allowed to stand in contact with freshly burnt lime to remove carbon dioxide, and then exhaustively fractionated. One preparation gave a large yield of Si_2H_6, but most of this was unfortunately lost before the experiments could be completed. A further quantity was obtained by decomposing lithium silicide as recommended by Moissan,* but the yield was less than for magnesium silicide. The mean density of the SiH_4 used in the earlier experiments measured at 25° and 690 mm. and calculated to N.T.P. without allowing for compressibility was 1·4462 gm./litre, corresponding with a molecular weight of 32·16, assuming 0·8% as the compressibility (calc. 32·09). Its density measured at —79·8° and 430 mm. and similarly calculated was 1·4556 gm./litre giving the compressibility at this temperature as 2·6%. The compressibility of Si_2H_6 at 26° was measured directly and found to be 2·6% and its density measured at 28° and 585 mm. and calculated to N.T.P. was 2·8618 corresponding with a molecular weight of 62·84 as compared with the accepted value 62·17. The gas thus contained a small quantity of impurity, probably a higher homologue.

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* 'C. R. Acad. Sci., Paris,' vol. 134, p. 1063 (1902).

Oxygen was prepared by heating pure potassium permanganate in a vacuum and passing the evolved gas over soda lime. After drying, the oxygen was fractionated at liquid air temperature. It was completely absorbed by phosphorus.

Nitrogen was made (A) by heating ammonium dichromate in a vacuum and liquefying the product. The gas was fractionated three times and appeared very pure. In case of contamination with oxides of nitrogen, some oxygen was added and the mixture sparked; the oxygen was removed with phosphorus and the residue again fractionated. No change was produced in the dielectric coefficient. (B) the oxygen was removed from air by means of phosphorus and the residue distilled several times to reduce the argon content, the later portions of the distillate being rejected.

Nitrous oxide was generated by heating pure ammonium nitrate in a vacuum and then passed over potassium hydroxide and phosphorus pentoxide. It was next condensed in a bulb at liquid air temperature and the incondensable gas pumped off. After warming, it was again condensed to remove adsorbed impurities and the process repeated several times until condensation was practically instantaneous. After rejecting the lowest boiling fraction, the remainder was divided into eight fractions with vapour pressures from 47 to 50 mm. at −115°. The refractive indices of the first and sixth fractions were the same to 1 part in 2000, but the actual value of $(n - 1)^{25}_{5460} \times 10^6$, (464·7) was lower than Cuthbertson and Metcalfe's figure 467·3. The gas was therefore again fractionated and the figure for the middle fractions found to be 465·4. On repeating the process no change was observed.

Nitric oxide was prepared by heating carefully purified nitroso-diphenylamine at 180°–190° as recommended by Marqueyrol and Florentin* who state that the product is free from nitrogen and other oxides. Only about 0·1% of impurity incondensable in liquid air was present, and after three fractionations the refractive indices of the first and last of six fractions were the same to 1 part in 1600.

Air was purified by passing over soda lime, circulating over phosphorus pentoxide and passing through a U-tube immersed in liquid air. Slow admission to the apparatus through soda lime and phosphorus pentoxide was found to be unsatisfactory, high values being obtained.

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* 'Bull. Soc. chim.,' vol. 11, p. 804 (1912).

Carbon dioxide was prepared (A), by heating sodium bicarbonate, and (B) by treating potassium bicarbonate with phosphoric acid and fractionating the product several times.

Carbon monoxide was prepared by heating sodium formate with phosphorus pentoxide in a vacuum, a method which was found more convenient than the customary sulphuric acid process. The gas was passed through a U-tube in liquid air which, when allowed to become warm at the end of the experiment liberated no trace of gas, indicating that the product was of high purity.

Sulphur hexafluoride was obtained by passing fluorine, generated by the electrolysis of fused potassium hydrogen fluoride in a copper vessel, over sulphur and allowing the product to stand over potassium hydroxide solution. The gas was fractionated at —115°, at which temperature its vapour pressure was 7 mm. Some air and CF_4 from the graphite electrode were removed and a high boiling residue was left, doubtless the Si_2F_{10} recently described by Whytelaw-Gray and Denbigh.* The value of $(n - 1)^{25}_{5460} \times 10^6$ was 708·5.

Silicon tetrafluoride was made by heating anhydrous silica (6 gm.) with potassium hydrogen fluoride dried at 110° (9 gm.) and a large excess of phosphorus pentoxide in an evacuated flask. The gases evolved were condensed in liquid air and the SiF_4 distilled at —115°, at which temperature its vapour pressure was 60 mm. Hydrogen fluoride was formed in appreciable quantities, but was easily separated, since it boils at 19°. Si_2F_6 recently described by Schumb and Gamble† even if formed along with SiF_4 has a negligible vapour pressure at —115°. The molecular weight of the gas deduced from microdensity determinations was 104·0 agreeing very nearly with the theoretical value 104·06 and the value of $(n - 1)^{25}_{5460} \times 10^6$ was 521·5.

Results.

Owing to the large number of measurements which have been made, amounting for carbon dioxide to 96, involving about 420 individual readings, it is not possible to give all the results in detail. The following tables show only typical values and many of the earlier experiments which are considered less accurate, or in which the purity of the gas was doubtful, have been omitted. Each figure is the mean of four or five readings or more if any tendency towards unsteadiness was observed. Most of the measurements were made with the condensers G_3 and G_4, some with G_2 and a few with G_1. They extended over a considerable period of time, G_1 being used up to the end of 1929, G_2 during 1930, G_3 for the next 18 months, and G_4 subsequently. The parallel method was employed in all the experiments with G_4 and in a few of those with G_3, the latter being marked "P" in the tables. In all other experiments the series arrangement was used.

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* 'Nature,' vol. 131, p. 763 (1933).

† 'J. Amer. Chem. Soc.,' vol. 54, p. 583 (1932).

In the later experiments special precautions were adopted for determining the effect of compressibility. Readings were taken alternately for high and low pressure ranges to eliminate possible temperature changes and the mean values plotted against the mean pressure. The value for zero pressure could thus be obtained. No deviation from linearity could be detected and it was therefore assumed that the compressibility correction was proportional to the mean pressure. The values for $\varepsilon - 1$ are calculated for 760 mm. and 25° from the measured values on the supposition that the gas is ideal. In the sixth column are given the values after applying the compressibility correction, these are proportional to $\varepsilon - 1$ divided by the actual density at the temperature of measurement. 25° has been adopted as a standard temperature in preference to 0° as measurements of dielectric coefficients and refractive indices are rarely made at the latter temperature. $p_1 - p_2$ is the range of pressure over which the measurements were made and p_m the mean pressure, both given to the nearest millimetre for brevity although actually measured to 0·05 mm. E is written for $(\varepsilon - 1)10^6$.

Table II.—Dielectric Coefficients reduced to 760 mm. and 25°.

No.	t.	$p_1 - p_2$.	p_m.	E.	$E_{p=0}$.	Remarks.
			Methane.			
1	26·4	635	343	801	800	G_1.
8	27·4	611	384	803	802	G_2. After refractionation.
11	24·4	581	368	803	802	G_2. ,, at −125°
12	29·1	625	388	804	803	G_3. ,,
13	29·3	627	389	803	802	G_3.
14*a*	−79·8	551	350	*808*	804	G_3.
14*b*	−79·8	553	351	*807*	803	G_3.
15	24·4	493	316	803	802	G_4.
			Ethane.			
5	26·4	615	394	1367	1355	G_2. Contained ethylene.
10	27·7	604	372	1375	1363	G_3.
11	−79·8	437	390	*1391*	1348	G_3.
12	−79·8	437	380	*1395*	*1353*	G_3.
13	27·8	607	373	1371	1359	G_3.
17*a*	19·9	487	317	1379	1369	G_4. Repurified.
17*b*	19·9	249	436	1383	1369	G_4.
17*c*	19·9	238	191	1371	1365	G_4.
18*a*	−79·8	393	266	*1396*	*1367*	G_4.
18*b*	−79·8	197	366	*1407*	*1367*	G_4.
18*c*	−79·8	197	169	*1385*	*1365*	G_4.

Table II—(continued).

No.	t.	$p_1 - p_2$.	p_m.	E.	$E_{p=0}$.	Remarks.
Propane.						
5*a*	19·6	314	548	2025	1971	G_3.
5*b*	19·6	313	237	1998	1975	G_3.
12	−79·8	79	57	*2011*	*1998*	G_3.
13	20·2	458	280	2000	1973	G_3.
16	21·8	517	404	2004	1966	G_4.
18*a*	−31·8	274	635	*2094*	*1971*	G_4.
18*b*	−31·7	656	445	*2056*	*1970*	G_4.
18*c*	−31·5	382	300	*2027*	*1968*	G_4.
18*d*	−31·4	239	153	*1998*	*1968*	G_4.
19*a*	−32·3	293	560	*2076*	*1967*	G_4.
19*b*	−32·3	308	259	*2021*	*1971*	G_4.
19*c*	−32·1	602	406	*2051*	*1972*	G_4.
20*a*	24·9	352	652	2027	1962	G_4.
20*b*	24·9	360	297	1992	1963	G_4.
20*c*	24·9	711	473	2009	1964	G_4.
Ethylene.						
3	23·3	485	304	1330	1324	G_2.
4	−79·8	403	260	*1346*	*1325*	G_2.
12	25·5	537	333	1328	1321	G_3. Refractionated.
13	25·5	337	203	1325	1321	G_3.
14	−79·8	472	300	*1341*	*1316*	G_3.
19	30·6	427	276	1322	1316	G_4.
20	29·3	700	464	1329	1319	G_4. Refractionated.
21*a*	−79·8	278	528	*1359*	*1316*	G_4.
21*b*	−79·8	282	248	*1338*	*1318*	G_4.
21*c*	−79·8	559	387	*1349*	*1317*	G_4.
22*a*	−79·8	345	633	*1369*	*1317*	G_4.
22*b*	−79·8	325	298	*1340*	*1316*	G_4.
22*c*	−79·8	670	470	*1353*	*1315*	G_4.
Propylene.						
10	24·1	262	159	2244	2225	G_2.
12	−79·8	96	61	*2545*	*2518*	G_2.
16	23·8	289	174	2272	2253	G_3. Refractionated.
18	26·2	423	256	2283	2255	G_3.
29	−79·8	110	66	*2447*	*2417*	G_3. Refractionated.
30	−79·8	108	66	*2436*	*2406*	G_3.
31	24·4	131	76	2267	2259	G_3.
32	−79·8	107	65	*2449*	*2420*	G_3.
33*a*	24·6	581	383	2290	2248	G_4.
33*b*	24·6	297	525	2306	2248	G_4.
33*c*	24·6	284	235	2274	2248	G_4.
34	22·8	578	382	2289	2247	G_4.
35*a*	−32·8	274	483	*2427*	*2331*	G_4.
35*b*	−32·8	254	218	*2373*	*2330*	G_4.
35*c*	−32·8	528	356	*2399*	*2329*	G_4.
36*a*	−32·3	273	483	*2425*	*2329*	G_4.
36*b*	−32·3	255	218	*2374*	*2331*	G_4.
36*c*	−32·3	529	356	*2405*	*2335*	G_4.

Table II—(continued).

No.	t.	$p_1 - p_2$.	p_m.	E.	$E_{p=0}$.	Remarks.
				Acetylene.		
6*a*	21·3	341	591	1224	1206	G_3.
6*b*	21·3	341	257	1214	1206	G_3.
7*a*	−79·8	256	557	*1277*	*1211*	G_3.
7*b*	−79·8	256	213	*1227*	*1202*	G_3.
8	−79·8	600	386	*1245*	*1199*	G_3.
9*a*	26·2	581	465	1221	1208	G_4.
9*b*	26·2	641	425	1219	1206	G_4.
10	−79·8	203	664	*1286*	*1208*	G_4.
11	−79·8	203	460	*1261*	*1207*	G_4.
12	−79·8	203	257	*1237*	*1207*	G_4.
13	−79·8	632	445	*1257*	*1205*	G_4.
15	25·3	311	195	1213	1207	G_4.
				Silicane.		
5	23·2	726	363	1674	1661	G_1.
8	−79·8	680	340	*1692*	*1654*	G_1.
9	−79·8	680	340	*1677*	*1639*	G_1.
10	25·4	645	322	1667	1656	G_1. Refractionated.
13	25·6	218	126	1674	1670	G_3.
14	−79·8	181	108	*1681*	*1669*	G_3.
19	21·6	553	340	1695	1683	G_3. New preparation.
20	21·8	455	276	1703	1693	G_3.
21*a*	−79·8	347	215	*1701*	*1677*	G_3.
21*b*	−79·8	209	285	*1710*	*1678*	G_3.
21*c*	−79·8	166	101	*1704*	*1693*	G_3.
22	22·0	450	275	1711	1701	G_3.
23*a*	26·1	316	590	1722	1701	G_4.
23*b*	26·1	326	266	1716	1707	G_4.
23*c*	26·1	645	426	1714	1699	G_4.
24	27·3	551	364	1699	1686	G_4. Refractionated.
25	25·9	592	390	1697	1683	G_4. Refractionated.
				Silicoethane.		
1	20·6	362	181	3259	3219	G_1.
2	25·0	175	87	3408	3388	G_2.
3*a*	−43·5	154	77	*3437*	*3382*	G_2.
3*b*	−43·5	93	46	*3449*	*3416*	G_2.
3*c*	−43·5	136	67	*3463*	*3415*	G_2.
4	26·2	212	124	3331	3303	G_2.
5	21·7	179	110	3463	3436	G_3. Trace H_2 removed.
7	21·9	179	105	3447	3421	G_3. Same gas.
8	29·3	239	151	3534	3500	G_4. Mixture of 2 samples.
9*a*	−33·5	107	187	*3608*	*3487*	G_4. Same gas.
9*b*	−33·5	101	82	*3538*	*3485*	G_4.
9*c*	−33·5	209	135	*3577*	*3496*	G_4.
10	26·8	210	133	3489	3460	G_4. Refractionated.
				Oxygen.		
5	21·5	620	384	491	490·5	G_3.
6	21·5	620	384	489	488·5	G_3.
7	−101·7	183	123	*492*	*480*	G_3.
9	−190·8	195	158	*493·5*	*480·5*	G_4.
10	28·3	616	404	486	485·5	G_4.
11	28·1	620	406	485·5	485	G_4.
12	−190·6	198	159	*494*	*481*	G_4.

Table II—(continued).

No.	t.	$p_1 - p_2$.	p_m.	E.	$E_{p=0}$.	Remarks.
Nitrogen.						
A 1	26·6	628	414	538·5	538·5	G$_4$.
A 2	26·6	568	444	537	537	G$_4$.
A 3	−190·7	313	346	*556*	*536*	G$_4$.
A 4	−188·1	462	383	*559·5*	*537·5*	G$_4$. Fractionated from charcoal.
A 5	22·0	712	474	539	538·5	G$_4$.
A 6	22·4	718	477	540	539·5	G$_4$. Treated with O_2 and P.
B 1	−190·3	509	424	*561*	*537*	G$_4$. "Atmospheric N_2."
B 2	−190·0	250	555	*569*	*537*	G$_4$.
B 3	−190·0	257	300	*554·5*	*537·5*	G$_4$.
B 4	21·4	622	488	537·5	537	G$_4$.
Air.						
3	24·5	624	381	531	530·5	G$_3$.
4	23·4	625	381	530	529·5	G$_3$.
6	25·9	565	440	529	528·5	G$_4$.
7	26·4	533	415	528·5	528	G$_4$.
8	20·8	713	477	538	(537·5)	G$_4$. Not dry.
9	20·6	686	458	528·5	528	G$_4$.
Nitrous Oxide.						
1	26·2	673	453	1030	1023	G$_4$.
2	27·4	659	441	1028	1021	G$_4$. Refractionated.
3*a*	−79·8	265	510	*1092*	*1060*	G$_4$.
3*b*	−79·8	273	240	*1075*	*1060*	G$_4$.
3*c*	−79·8	538	375	*1083*	*1059*	G$_4$.
4	25·6	683	456	1032	1025	G$_4$.
5	−32·9	626	425	*1052*	*1039*	G$_4$.
6*a*	−79·8	562	392	*1084*	*1060*	G$_4$.
6*b*	−79·8	277	534	*1092*	*1060*	G$_4$.
6*c*	−79·8	285	253	*1074*	*1059*	G$_4$.
Nitric Oxide.						
1	25·2	711	474	593·5	593	G$_4$.
2*a*	−79·8	309	546	*631·5*	*627*	G$_4$.
2*b*	−79·8	277	252	*629*	*627*	G$_4$.
2*c*	−79·8	586	407	*630*	*627*	G$_4$.
3	25·2	673	447	592	591·5	G$_4$.
4	−79·8	637	445	*631*	*627·5*	G$_4$.
5	25·0	679	452	596	595·5	G$_4$.
Carbon Dioxide.						
A 12	25·5	628	398	904	899	G$_2$.
A 18	*−79·8*	446	276	*916*	*900·5*	G$_3$.
A 19	20·1	678	421	908	902·3	G$_3$.
A 25	29·2	583	365	907	902·5	G$_3$.
A 31	24·5	558	347	909	905	G$_3$.
A 34	25·2	445	287	904	900·5	G$_4$.
A 35	23·6	448	287	905	901·5	G$_4$.
B 17	−79·8	508	322	*919*	*901*	G$_3$.
B 18	−79·8	387	242	*913*	*899*	G$_3$.

Table II—(continued).

No.	t.	$p_1 - p_2$.	p_m.	E.	$E_{p=0}$.	Remarks.
			Carbon Dioxide—(continued).			
B 19	26·2	446	273	910	907	G_3.
B 32	26·6	707	450	904·5	898·5	G_3, P.
B 35	25·8	567	380	905·5	901	G_4.
B 36	−79·8	461	318	*917*	*898·5*	G_4.
B 37	−79·8	240	430	*923·5*	*898·5*	G_4.
B 38	−79·8	220	197	*911*	*899·5*	G_4.
B 39	−79·8	173	115	*909*	*902·5*	G_4.
B 41	23·5	692	461	906·5	901	G_4.
B 42*a*	−79·9	234	414	*926*	*902*	G_4.
B 42*b*	−79·9	214	189	*911*	*900*	G_4.
B 42*c*	−79·9	447	307	*917*	*899*	G_4.
B 42*d*	−79·9	195	130	*907·5*	*900*	G_4.
B 43*a*	23·9	700	465	908	902·5	G_4.
B 43*b*	23·9	294	186	904	902	G_4.
			Carbon Monoxide.			
1	24·4	626	390	635·5	635·5	G_3, P.
2	24·1	626	390	636	636	G_3.
3	24·2	626	390	635·5	635·5	G_3.
4	−191·1	367	250	*725*	*703*	G_3.
5	−190·6	539	381	*736·5*	*703*	G_3.
6*a*	−190·5	245	535	*746·5*	*699*	G_3.
6*b*	−190·5	296	260	*723*	*700*	G_3.
8	−188·9	605	432	*731*	*693*	G_3.
9*a*	−188·0	347	240	*717*	*696*	G_3.
9*b*	−188·0	176	120	*706*	*696*	G_3.
10	25·4	706	475	635·5	635	G_4.
			Sulphur Hexafluoride.			
5	−79·8	172	105	*2062*	*2034*	G_3.
6	25·8	204	122	2039	2032	G_3.
8	−79·8	172	105	*2044*	*2016*	G_3.
9	26·9	206	122	2041	2034	G_3.
11	−79·8	172	105	*2051*	*2023*	G_3.
12	25·8	205	122	2041	2034	G_3.
13	25·8	292	176	2034	2023	G_3. Early fraction added.
15	27·5	677	425	2049	2023	G_3, P. Refractionated.
16	28·1	676	425	2050	2024	G_3.
17	25·2	531	345	2051	2030	G_4.
			Silicon Tetrafluoride.			
7*a*	28·2	672	390	1710	1698	G_3, P.
7*b*	28·2	294	560	1714	1696	G_3.
7*c*	28·2	334	245	1704	1696	G_3.
8*a*	−79·8	552	350	*1721*	*1670*	G_3.
8*b*	−79·8	224	512	*1741*	*1667*	G_3.
8*c*	−79·8	317	235	*1705*	*1671*	G_3.
11	25·4	595	470	1702	1687	G_4.
12	−79·8	518	425	*1739*	*1677*	G_4.
13	−79·8	259	558	*1759*	*1678*	G_4.
14	−79·8	259	295	*1721*	*1678*	G_4.
15	−79·8	602	495	*1754*	*1682*	G_4.
16	−79·8	196	700	*1785*	*1683*	G_4.
17	−79·8	192	507	*1761*	*1687*	G_4.
18	−79·8	212	300	*1725*	*1681*	G_4.

Table III gives the actual values adopted for the compressibilities, the figures representing the percentage correction for a pressure change from 0 to 1 atmosphere or a mean pressure of 380 mm.

Table III.—Compressibility corrections % for mean p. 380 mm.

	25°.	−32°.	−80°.	−190°.
CH_4	0·20	0·4	0·7	—
C_2H_6	0·88	—	3·0	—
C_3H_8	1·85	3·70	7·4	—
C_2H_4	0·60	—	2·35	—
C_3H_6	1·85	3·2	7·0	—
C_2H_2	0·94	—	3·6	—
SiH_4	0·80	—	2·7	—
Si_2H_6	2·60	7·0	—	—
O_2	0·08	—	—	5·2
N_2	0·04	—	—	3·8
N_2O	0·55	1·1	2·3	—
NO	0·09	—	0·47	—
CO_2	0·50	—	2·4	—
CO	0·04	—	—	4·9
SF_6	1·15	—	5·0	—
SiF_4	0·72	—	3·3	—

The values at 25° for CH_4, C_2H_2, O_2, N_2, NO, and CO are taken from tables, the figures for 25° when not available being obtained from those at 0° by multiplying by the factor 0·8. For C_2H_4, N_2O, and CO_2 the recently published values of Cawood and Patterson* have been adopted. The values for C_3H_8, C_3H_6, and SiF_4 were determined by measuring the dielectric coefficients at two or more pressures and the results were confirmed by refractometric measurements. The figures for SiH_4, Si_2H_6, and SF_6 were determined directly in an apparatus specially constructed for the purpose which will be described elsewhere. The densities of SiH_4 and SF_6 were measured at 25° and −80° and the compressibilities deduced from the results.

The remaining low temperature values, except those for CH_4 and O_2, were determined by dielectric coefficient measurement. The figures for CH_4 at −80° and O_2 at −190° were obtained by extrapolation and the accuracy of the latter is somewhat doubtful. It is, however, of the order to be expected from comparison with the values for N_2 and CO_2.

A comparison of the results obtained with different condensers after reduction to zero pressure shows a close agreement in the absolute values. This is particularly satisfactory since the method of measurement employed with G_4 and the associated calibrations were based on entirely different systems to those used with the other condensers. Taking CO_2 as an example, the mean of the values obtained with G_2 (given in Part I and not included in Table II) was 904, or on reduction to zero pressure 899. The mean value with G_3 and the series connection, including results not given in the table, was 904 and with G_4, 901. The figure 944 at 16° or 910·5 reduced to zero pressure at 25° originally obtained by one of us,* was observed with the condenser G_1 and was not corrected for condenser distortion or change in the value of the measuring condensers with frequency. The corrections for these factors have now been determined and amount to —5 and —6 units respectively, giving a final value of 899·5. The results with G_2 are subject to an undesirably large distortion correction (+16) and the capacity of G_3 was rather small. The values obtained with G_4 in addition to being far more consistent among themselves are probably the most accurate in absolute magnitude owing to the uncertainty attending the use of the series method mentioned earlier; most of the measurements were, moreover, made at the end of a series with a view to explaining any discrepancies observed in previous experiments and the gases were in their highest state of purity. In deducing mean values, therefore, the results with this condenser have been taken as standard.

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* 'J. Chem. Soc.,' p. 619 (1933).

The values for the individual gases call for little comment. *Methane* gave very consistent values and the results at low temperature were practically identical with those at 25°. *Ethane* when first prepared contained ethylene and the first five results given are somewhat low on this account. It has no moment. *Propane* has very large compressibility coefficients and an error in their determination may account for the slight difference between the values at the two higher temperatures. A small error may also arise from the use of the phenetol bath, the temperature of which was not as steady as for CO_2. The value (experiment 12) recorded at —80° was obtained at a pressure only 25 mm. greater than the vapour pressure and the high value may be due to adsorption. Two other experiments at a pressure 5 mm. greater than No. 12 gave the values 2008 and 2010 when reduced to zero pressure. In all three results the experimental error was large owing to the low pressure and they cannot be taken to indicate the existence of a moment.

The results for *ethylene* are in good agreement, the condenser G_3 giving as for carbon dioxide values about 1 part in 300 higher than those when G_4 was used. *Propylene* was a difficult gas to purify and early values were low at room temperature and very high at —80° (Nos. 10 and 12), a rather unusual result, the reason for which is not evident. After an exhaustive series of fractionations, a number of values ranging from 2253 to 2259 was obtained irrespective of the fraction of gas employed. As the vapour pressure of the gas at —80° was 134 mm. the values at this temperature are not very reliable. The results with G_4 are in good agreement and again lower than those with G_3. This gas has a moment. *Acetylene* was easily obtained in a pure condition and gave concordant values.

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* Watson, *loc. cit.*

The early values for *silicane* were distinctly lower than those obtained later, doubtless owing to variations in the purity of the gas. Although the gas is stable when kept for considerable periods in contact with mercury, there appears to be a slight tendency to form higher homologues in the presence of tap-grease and these are not easy to remove. The high values in experiment 23 may be due to this cause. The two final values are probably the most accurate, but less reliance can be placed upon them than for other gases. The low temperature values are not very consistent, but suffice to show that the gas has no appreciable moment. The results for *silicoethane* are worse, the early determinations (2 and 3) made with gas, the density of which was measured, being very much lower than those made with a mixture of two preparations which were found by the refractometer to differ slightly in composition. The early values were not very consistent and are subject to a large experimental error and so the figure 3450 has been adopted as the final result. A comparison of the two pairs of experiments 2 and 3 and 8 and 9 which were made with the same gas on consecutive days shows that the moment is negligible within the limits of experimental error. All these results must be regarded as provisional until a larger quantity of gas can be obtained.

Oxygen gave values which, although concordant, were several units lower at liquid air temperature than at room temperature, an unusual result. Owing to the low vapour pressure, the compressibility at —190° could not be determined directly, but to make the results at the two temperatures equal it would have had to be 2·8% instead of 5·2 the calculated value. The former figure is certainly too low and thus the reason for the discrepancy is not clear. It may be due to experimental error, which was rather high for the low pressures employed. The figures for *nitrogen* were consistent and practically equal at the two temperatures. *Air* was not measured at low temperatures as the results did not appear to be of interest. Experiment 8 is given as an illustration of the ease with which high values may be obtained if insufficient care is taken in drying. In this the gas was drawn from a desiccator containing sticks of caustic potash and phosphorus pentoxide in which it had stood for some days and passed slowly through tubes of soda lime and phosphorus pentoxide. It was only after passing through a U-tube immersed in liquid air and again over phosphorus pentoxide that the normal figure of experiment 9 was obtained.

Nitrous oxide gave very concordant values, but as these indicated that the gas had a moment, the experiments were repeated 4 months later with an additional determination at the temperature of melting phenetol. The results (4–6) were in good agreement with those previously obtained, although the value at room temperature was slightly higher than before. This may be due to slight contamination with water vapour on standing. *Nitric oxide* also gave concordant values which were confirmed later (4, 5), the room temperature value again being slightly higher than before, possibly for the same reason.

The results obtained with *carbon dioxide* have been discussed already. *Carbon monoxide* gave varying values at liquid air temperature because the temperatures employed were not all the same and the gas has an appreciable moment. It may be calculated that a change of 2·5° alters E by 3 units and this brings the results into sufficiently good agreement.

The values for *sulphur hexafluoride* at low temperature appeared slightly lower than at 25°. This may be due to experimental error, but it appears certain that the gas has no moment. The early experiments with *silicon tetrafluoride*, although giving very consistent values, indicated that E was distinctly lower at the lower temperature, an effect which might be due to the presence of a condensable impurity. No such impurity could be detected, however, as a repetition of experiments 7 and 8 after refractionation gave identical values and successive fractions of gas had the same dielectric coefficient. With condenser G_4, the values approached each other more nearly, but there still appeared to be a difference. It is difficult to say whether this is a real effect or an experimental error in the compressibility correction, which is large.

The final mean values of E and the polarizations calculated by means of the formula $P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{m}{d} = 0 \cdot 008155 \, E_0$ are shown in Table IV. The first column gives the value which would be obtained in an actual measurement at 25° for a pressure range of 0–1 atmosphere. These figures are calculated by means of the compressibility from those in the second column which represent the limiting values of E (calculated for 25° and 0–1 atmosphere by means of the simple gas law) at zero pressure; that is to say, the values which would be found if the gases were perfect. The limiting values at lower temperatures are given in the following columns; actual values have not been shown since they are often meaningless, the gases liquefying below 1 atmosphere pressure. If required they may be calculated by means of the compressibilities given in Table III. In order to obtain the mean values, all the available data have been taken into account, not merely the figures given in the tables, and the results with condenser G_3 have been reduced by 3 parts in 900 and those with G_1 and G_2 increased by 1·5 and 2 parts in 900 in order to make the mean absolute values for CO_2 agree as explained on p. 576.

Table IV.—Mean Dielectric Coefficients and Polarization.

Gas.	E^{25}_{0-1}	$E^{25°}_{0}$	$E^{-33°}_{0}$	$E^{-80°}_{0}$	$P^{25°}$
CH_4	804	801	—	801	6·53
C_2H_6	1380	1368	—	1306	11·16
C_3H_8	2000	1964	1970	(1990)	16·02
C_2H_4	1325	1317	—	1317	10·74
C_3H_6	2289	2248	2331	2411	18·33
C_2H_2	1217	1206	—	1206	9·84
SiH_4	16916	1683	1680	—	13·72
Si_2H_6	3540	3450	(3450)	—	28·10
O_2	486	486	—	480*	3·96
N_2	538	538	—	537*	4·39
Air	528	528	—	—	4·31
N_2O	1028	1022	1039	1060	8·33
NO	593	592	—	627	4·83
CO_2	906	901	—	900	7·35
CO	634	634	—	697*	5·17
SF_6	2049	2026	—	2018	16·51
SiF_4	1702	1690	—	1681	13·78

* −190°.

Most of the gases tested have been examined previously by other observers and a comparison of results is interesting. Owing to the different methods of presentation adopted and the varying temperatures at which results are given it is often difficult to judge the merits of any particular series. In Table V all the available data are shown calculated for 25° and 0–1 atmosphere, the figures being actual values; that is to say, those corresponding with column 1 of Table IV which is repeated for comparison. Where the gas has an electric moment, the author's value at 25° has been selected or obtained by interpolation. Where measurements have been made at a lower room temperature, the results, strictly speaking, should be corrected for the difference in compressibility at the two temperatures, but for most this correction is very small and it has not been applied.

In this table the results are entered in chronological order. Those of Boltzmann are of little more than historical interest, but it is interesting to note that Klemenčič's values mostly agree with those more recently determined. Among

Table V.—Values of E at 25° and 0–1 atmospheres.

Gas.	Tab. IV.	Bo.*	K.	T.	Ro.	Re.	Z.	Fr.	Br.	Fo.	Mc.
CH_4	804	865	873	—	—	810	—	—	—	—	—
C_2H_6	1380	—	—	—	—	—	1379	—	—	—	—
C_3H_8	2000	—	—	—	—	—	—	—	—	—	1996
C_2H_4	1325	1202	1334	—	—	—	1322	—	—	—	—
C_3H_6	2289	—	—	—	—	—	—	—	—	—	2257
C_2H_2	1217	—	—	—	—	—	1227	—	—	—	—
O_2	486	—	—	—	501	—	474	465	—	—	—
N_2	538	—	—	571	555	—	532	509	—	493	—
Air	528	540	—	528	—	540	524	495	—	493	533
N_2O	1028	1058	907	—	1030	—	—	—	1040	—	—
NO	593	—	—	—	—	—	—	—	—	—	598
CO_2	906	867	903	—	906	900	903	868	920	882	906
CO	634	632	637	—	—	625	646	—	651	—	—
		S. & W.	G.								
N_2O	—	1004	962								
		P.	J.	B.	C.	B. & S.	S.	G.			
Air	—	537	501	566	544	540	534	530			
CO_2	—	P. 911	S. 904	J. 1013							

*B.	Bedeau, 'C. R. Acad. Sci., Paris,' vol. 174, p. 380 (1922).
Bo.	Boltzmann, 'SitzBer. Akad. Wiss. Wien,' vol. 69, p. 795 (1874).
Br.	Braunmühl, 'Phys. Z.,' vol. 28, p. 141 (1927).
B. & S.	Bryan and Saunders, 'Phys. Rev.,' vol. 32, p. 302 (1928).
C.	Carman and Hubbard, 'Phys. Rev.,' vol. 29, p. 299 (1927).
Fo.	Forro, 'Z. Physik,' vol. 47, p 430 (1928).
Fr.	Fritts, 'Phys. Rev.,' vol. 23, p. 345 (1924).
G.	Ghosh and others, 'Z. Physik,' vol. 58, p. 200 (1929); 'Nature,' vol. 124, p. 13 (1929).
J.	Jona, 'Phys. Z.,' vol. 20, p. 14 (1919).
K.	J. Klemenčič, 'SitzBer. Acad. Wiss. Wien,' vol. 91, p. 712 (1885).
Mc.	McAlpine and Smyth, 'J. Amer. Chem. Soc.,' vol. 55, p. 453 (1933).
P.	Pohrt, 'Ann. Physik,' vol. 42, p. 569 (1913).
Re.	Reigger, 'Ann. Physik,' vol. 59, p. 753 (1919).
Ro.	Rohmann, 'Diss.' Strassbourg (1910).
S.	Stuart, 'Z. Physik,' vol. 47, p. 457 (1928).
S. & W.	Schwingel and Williams, 'Phys. Rev.,' vol. 35, p. 855 (1930).
T.	Tangl, 'Ann. Physik,' vol. 26, p. 59 (1908).
Z.	Zahn and others, 'J. Amer. Chem. Soc.,' vol. 47, p. 2501 (1925), C_2H_6, etc.; 'Phys. Rev.,' vol. 27. p. 455 (1926), O_2, N_2, NO, CO_2; *ibid.*, vol. 32, p. 497 (1928), CO.

the modern determinations, those of Fritts are distinctly low, while Forro's figures are not reliable, the values for nitrogen and air being the same. Zahn's values agree closely with those we have determined, being a few units lower throughout except for acetylene and carbon monoxide. His value for air, 524, is slightly higher than 520, the figure calculated from the individual determinations for oxygen and nitrogen. McAlpine and Smyth's values for four of the five gases they examined are close to our figures, but the value for proplyene appears low. Actual dielectric coefficients are not given in their paper and the figures in Table IV have been calculated from the polarizations, but the exact compressibility correction they have applied is uncertain. Rohmann's values for nitrous oxide and carbon dioxide are almost identical with ours, but his figures for oxygen and nitrogen are much lower.

In view of the number of measurements which have been made using air as a medium for condenser calibration it is interesting to note the very considerable variations in the values given by different observers for this substance. It has been mentioned already that unless very special precautions are taken high values may be obtained owing to the presence of moisture. McAlpine and Smyth did not dry their gas with liquid air and the somewhat high value as compared with CO_2 may be due to this. Bryan and Saunders' result may be high partly for the same reason and partly owing to the fact that lead inductance corrections were not applied. Although these authors state that this correction was negligible, the figures they give indicate that it was not entirely so, and from the dimensions of the coils they used (private communication) it is almost certain that an appreciable correction should have been applied which would have lowered the value. Apart from its being a mixture, air is not a good calibrating medium owing to its low dielectric coefficient which, in addition to being somewhat difficult to measure, is liable to a large proportional error from condenser distortion. As indicated in I, carbon dioxide is a more suitable gas for the purpose and this is borne out by the greater concordance between the results shown in Table V.

There appears to be no simple relation between the molecular polarization and the molecular weight of these gases, although in general the heavier gases have a larger polarization. If van der Waal's co-volume b is considered as suggested by Debye,* a certain correlation is apparent; for example, the value of $10^4\,b/P$ or more strictly of $10^4\,b/A$, A being the first term in Debye's equation, is about 2·4 for the hydrocarbons, slightly more for CO_2 and NO and 3·5 to 3·9 for CO, O_2, and N_2. SiH_4 and SiF_4 are interesting as these gases have almost identical dielectric coefficients in spite of the great difference in their molecular weights, while the values of b are nearly coincident, so that $10^4 b/P$ is 1·9 for both.

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* "Polar molecules," p. 15 (1929).

Although the values of this ratio do not differ very widely in the cases under consideration, if the inactive gases are considered the variation is much greater, the figures being for helium 13, neon 7·6, argon 3·3, krypton 2·8, and xenon 2·3. It is evident, therefore, that there is no simple relation between the polarization and the co-volume and that measurements must be extended to more gases before the theoretical significance of P can be determined.

The Electric Moment.

From Table IV it may be seen that the only gases which have an electric moment detectable by the method of measurement employed are propylene, the two oxides of nitrogen and carbon monoxide. The existence of a moment in carbon dioxide has been discussed frequently and the present figures support the statement of Stuart that it is negligible. Sulphur hexafluoride has no moment, a fact of interest since its exact configuration is not known. It is intended to measure its parachor, the value of which should throw further light on the subject. Table VI gives the values of A and B in Debye's equation $P = A + B/T$ derived from the figures in Table IV and of μ calculated from the expression $B = 4\pi N\mu^2/9k$, or when N, Avogadro's number, is taken as $6\cdot06 \times 10^{23}$ and k, Boltzmann's constant as $1\cdot372 \times 10^{-16}$, from the expression $10^{18}\,\mu = 0\cdot01272\sqrt{B}$.

Table VI.—Values of A, B, and μ.

	T.	A.	B.	$\mu \times 10^{18}$.	Other observers.
C_3H_6	298–240	15·51	840	0·37	0·35 (Mc.).*
	240–193	16·35	640	0·32	
	Mean	15·90	730	0·34	
N_2O	299–240	7·76	170	0·17	0·25 (Br.); 0·00 (G.); 0·05 (S. & W.).
	240–193	7·77	168	0·17	
	Mean	7·77	169	0·17	
NO	298–193	4·31	156	0·16	0·07 (Mc.).
CO	298–83	4·98	59	0·10	0·12 (Br.); 0·11 (Z.); 0·118†.

* For references see under Table V.

† Weight, 'Phys. Z.,' vol. 22, p. 643 (1921).

It will be observed that the two sets of values for propylene at different temperatures are not identical. If E at −33° were 2322 instead of 2331, the figures would coincide, A becoming 15·88 and μ 0·34 × 10^{-18}, agreeing closely with McAlpine and Smyth's value. The difference of 9 units is slightly larger than would be expected from the general concordance of the experiments, but it is not of sufficient magnitude to be accepted as evidence of the incorrectness of Debye's equation. The mean value given is calculated by the method of least squares.

The values for nitrous oxide are of interest since it is frequently assumed that this gas has no moment. The determination at −33° for this agrees very closely with the results at the other two temperatures and there seems no reason for supposing that there is a large experimental error. The two measurements of compressibility were concordant and may be taken to include any correction due to adsorption since this would be approximately proportional to the pressure. It has been found by Grunmach* that liquid nitrous oxide has the same molecular weight as the gas and hence polymerization at low temperatures is unlikely; even if it did occur the degree of polymerization would be proportional to the pressure and so allowed for on extrapolating to zero pressure.

Schwingel and Williams give 0·05 as an upper limit for the moment and state that they consider the correct value to be zero. Their results are not very concordant, but if B is calculated from them by the method of least squares its value is found to be 76 corresponding with 0·11 for the moment, so that their deduction appears incorrect. Ghosh and Mahanti's figures similarly treated give $B = 47$ and $\mu = 0{\cdot}08 \times 10^{-18}$.

The result for nitrous oxide is distinctly higher than that of McAlpine and Smyth, but for carbon monoxide the agreement between different observers is much closer possibly owing to the larger range of temperature available with this gas.

The value of the moment for propylene is 0·34 approximating to the figure 0·37 determined by Smyth and Zahn (*loc. cit.*) for α-butylene. Calculations of these quantities from known values for the different linkages in the molecule have been made, but they appear to require certain assumptions which are not altogether justifiable. It is advisable, therefore, to defer this matter until results are available for the higher hydrocarbons, experiments with which are in progress.

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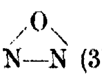
* 'SitzBer. Preuss. Akad. Wiss., Berlin,' No. II, p. 1198 (1904).

The Structure of Nitrous Oxide.

During the last few years numerous papers dealing with the structure of the N_2O molecule have been published, but the uncertainty as to whether the gas has a small moment or none has been an obstacle to definite conclusions.

If our results, supported by those of Schwingel and Williams, may be taken as correct, they should make some contribution to the solution of this difficult problem.

The three structures for N_2O commonly regarded as possible are N—O—N (1) N—N—O (2) and  $\overset{O}{N—N}$ (3), the lines indicating merely which atoms are connected and not the nature of the linkage. Those who adopt formula (1) have almost invariably considered the molecule linear, but since the gas has a moment this cannot be so and the molecule must be bent, even if only through a small angle. Such a molecule would be less symmetrical than the linear model and might thus resemble more closely the unsymmetrical formula (2) which has been regarded as the most probable by a large number of observers.

One of the first to suggest formula (2) was Langmuir* on the ground of the difference in the melting points of CO_2 and N_2O, all the other common physical properties being nearly identical. This deduction appears scarcely legitimate by itself since it is not possible to determine the effect of a slight bending of the molecule on the melting point and, moreover, although the electronic configuration of $:\ddot{O}::C::\ddot{O}:$ and $:\ddot{N}::O::\ddot{N}:$ in the gaseous form may be the same it does not necessarily follow that the inter-molecular attraction in the solid is identical.

De Smedt and Keesom† have examined the crystal structure of solid N_2O and state that their results agree with a straight molecule situated on the diagonal of a cube with oxygen at the centre and the distance O—N = 1·15 A. It appears likely, however, that a molecule N—N—O would give an almost identical pattern. It is not possible to settle the question without access to detailed experimental results which do not appear to have been published. Similarly the atomic distance in the gas N — N = 2·38 A. measured by Wierl‡ might equally well be the distance between the outer N and O in formula (2).

From an examination of the infra-red spectrum Snow§ deduced that the molecule had form (1) and was straight, the distance N—O being 1·02 A.

* 'J. Amer. Chem. Soc.,' vol. 41, p. 1545 (1919).

† 'Comm. Phys. Lab. Univ. Leiden,' vol. 16, supp. 53a (1924).

‡ 'Ann. Physik,' vol. 8, p. 521 (1931).

§ 'Proc. Roy. Soc.,' A, vol. 128, p. 294 (1930).

and N—N 2·04 A., while the moment of inertia was $54 \cdot 5 \times 10^{-40}$. Plyler and Barker* after making more detailed measurements concluded that the molecule, although straight, was unsymmetrical.

Interpretations of the Raman spectrum are also discordant. Snow considered that the data support his formula (1), Raman† states that (2) is the most probable arrangement, while Kohlrausch‡ favours the triangular model (3) with a vertical angle of 140°. More recently Langseth and Nielson§ have found additional lines which they consider to confirm formula (2).

The Kerr constant data examined by Stuart and Volkmann|| are interesting. The anisotropic term $K_2 = 0 \cdot 4$ corresponds with a moment of 0·15, practically the observed value. A positive value of K_2 can only arise from the unsymmetrical linear model (2), a bent molecule giving negative values. The authors point out, however, that the errors of experiment and calculation are large, so that too much reliance must not be placed on this result.

Several authors consider that the chemical reactions of the molecule support formula (2) and in particular this structure is confirmed by Herzberg¶ from a study of the nature of the unimolecular decomposition and by Bailey** from the fact that the heat of formation is the mean of those calculated for N—N and N—O.

The problem has been investigated from the point of view of quantum mechanics by Pauling†† who takes into consideration the moment of inertia deduced by Plyler and Barker and shows that this corresponds with structures resonating between the two forms $:\ddot{N}::N::\ddot{O}:$ and $:N:::N:\underset{..}{\ddot{O}}:$.

It is not possible in the present communications to discuss or even to mention all the papers which have been written on this subject, but the extracts given show the preponderance of evidence in favour of the linear unsymmetrical formula.

One of the difficulties connected with this configuration is the small value of the observed moment. The moment of nitrosobenzene is 3·2 and the angle between the C—N and N=O bonds is probably 125°. Adopting the approxi-

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* 'Phys. Rev.,' vol. 38, p. 1827 (1931).

† 'Malaviya Commem.,' p. 759 (1932).

‡ "Der Smekal-Raman Effect," p. 182 (1931).

§ 'Nature,' vol. 130, p. 92 (1932).

|| 'Z. phys. Chem.,' B, vol. 117, p. 429 (1932).

¶ 'Z. phys. Chem.,' B, vol. 17, p. 68 (1932).

** 'Nature,' vol. *130*, p. 239 (1932).

†† 'Proc. Nat. Acad. Sci., Wash.,' vol. 18, p. 498 (1932).

mate method of Hammick, New, Sidgwick, and Sutton,* the contribution of the C—N bond is 1·3 and hence the moment of the N=O group is 2·3. If the electronic distribution in the N=O bond of N=N=O were the same as in the nitroso group and the group N=N were symmetrical, the resulting moment would be 2·3, far higher than the observed value. That the latter group is unsymmetrical may, however, readily be seen if the formula be written $N \overset{\leftarrow}{=} N{=}O$ or $N^{-}{=}N^{+}{=}O$ according to Fowler,† indicating the transfer of an electron from one nitrogen atom to the other. Since the inter-atomic distance is 1·15 A. such a transfer would give rise to a moment of 5·5‡ and the resultant would be 3·2, again much more than the observed value. The figure 5·5 is undoubtedly too high, as any complete transference would affect the rest of the molecule and reduce the resulting moment, the magnitude of the effect not being readily calculable. It is, however, sufficient to note that moments of opposite sign are associated with the two halves of the molecule and it is not improbable that they should nearly cancel one another.

The cases of $C \overset{\leftarrow}{\equiv} O$ and NO are very similar. Hammick and co-workers assume a moment of 4·1 for six shared electrons in the former gas and 5·5 in the opposite direction for a transferred electron. The resultant 1·4 is still larger than the observed value. The latter gas is of an unusual nature owing to the presence of an odd electron. If it be considered that the bond is made up of 5 shared electrons, the formula can be written $:N\overset{\curvearrowleft}{=}O:$ the bent arrow indicating a single electron bond. For purposes of calculation this may be considered as having half the moment of a single N—O bond, *i.e.*, 0·6, together with half the moment resulting from a transferred electron, *i.e.*, 2·75. The total moment of the molecule would thus be 2·3 + 0·6 − 2·75 or 0·15, very nearly the experimental value. In all cases, however, these figures are purely qualitative and are intended merely to suggest the manner in which these small moments may arise.

The possibility of a slightly bent N—O—N molecule has received very little consideration and it is not improbable that it would sometimes fit observed facts as well as form (2). A rough estimate of the angle of such a molecule can be made by considering the O, N linkage to consist of four shared electrons with moment 2·3 and a transferred electron with moment 5·5 in the opposite direction. The resultant would be 3·2. The angle required to give the whole molecule a resulting moment of 0·17 would be 177°. This figure probably represents a maximum value since the analogous calculation for $N \overset{\leftarrow}{-} N{=}O$ leads to too high a value for the moment of N_2O and thus the moment of each $N \overset{\leftarrow}{-} O$ bond in $N \overset{\leftarrow}{-} O \overset{\rightarrow}{-} N$ is likely to be less than 3·2. It has been pointed out by Fowler and others that in unsaturated structures such as N—O—N and N═N—O the bonds would be at an angle of 90° (or 110°) or 125° while the configuration $N^{-}{=}{}^{+}O^{+}{=}N^{-}$ would be straight. The possibility of a molecule with an angle not far from 177° being stable is therefore somewhat doubtful, while if the value were 125° or even 140° according to Kohlrausch it would be detected by means of the infra-red spectrum. In this connection attention may be drawn to the recently published work of Ibbs and Wakemann* who have suggested that above 145° the CO_2 molecule may assume a bent form. It is proposed to measure the moment of this gas at high temperature as a small moment might indicate the existence of a stable symmetrical molecule with a large angle between the bonds. Unless this is found there is little evidence to support formula (1) and hence there seems no alternative but acceptance of the arrangement N—N—O, the electronic structure being either simple or an equilibrium as suggested by Pauling.

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* 'J. Chem. Soc.,' p. 1881 (1930).

† "Chemistry at the British Association," p. 242 (1932).

‡ *Cf.* Smyth, "Dielectric Constant and Molecular Structure," p. 64 (1931).

In conclusion, we wish to express our best thanks to Dr. M. A. Govinda Rao for much assistance in discussing the structure of the N_2O molecule.

Summary.

(1) The dielectric coefficients of 17 gases have been measured at two and for some at three temperatures and their electric moments deduced from the results.

(2) Compressibilities have been directly determined by making measurements at different pressures.

(3) The dielectric coefficient of helium has been redetermined in order that the result may be used for measuring the deformation of a condenser with pressure.

(4) The construction and calibration of a precision variable condenser capable of measuring a change in capacity of 0·4 μμF. with an accuracy of 0·0001 μμF. has been described.

(5) The results have been compared with those of previous observers, satisfactory agreement being obtained in certain cases.

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* 'Proc. Roy. Soc.,' A, vol. 134, p. 636 (1932).

(6) Of the gases investigated only propylene, carbon monoxide, nitrous oxide, and nitric oxide have measurable electric moments. The existence of such a moment for nitrous oxide has been considered in relation to the structure of the molecule, and the possibility of a slightly bent symmetrical molecule discussed. A tentative explanation for the small moment of the unsymmetrical linear form has been put forward which would enable this type of molecule to be accepted as most probable in conformity with the results obtained by other methods.

The Mean Lives of Excited Neon Atoms.

By J. H. E. Griffiths.

(Communicated by F. A. Lindemann, F.R.S.—Received September 30, 1933.)

Introduction.

Since the first experiments by Wien many methods have been used to find the average lives of the excited states of different atoms. Most of these methods are applicable to particular atoms only, and the amount of reliable information in this field is still surprisingly meagre.

The method described here depends in effect on the measurement of the lag which exists between the excitation and emission of light from atoms in a high-frequency discharge. This lag, or rather the quantity actually measured, is itself a first approximation to the average life τ of the state concerned, and it is shown later how a more accurate value of τ may be deduced from it. Results are given for six excited states of the neon atom, but the method may be used for any substance whose spectrum can be obtained from a high-frequency discharge. The values of τ for neon range from $3 \cdot 9$ to $20 \cdot 10^{-8}$ seconds, and it is shown that lines originating from the same upper level lead to the same value of τ for that level.

Of the previous methods that of Wien is well known, but mention must be made of a method used by Hupfeld[*] and improved from the theoretical side by Duschinsky.[†] Here two Kerr cells are used operated by a high frequency potential. The first cell modulates the light which excites the resonance radiation in sodium vapour, this is then analysed by the second cell. Calibration is effected by replacing the sodium vapour by a mirror arranged to produce a light path of variable length. This method can only be used where a convenient resonance line is available.

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[*] 'Z. Physik,' vol. 54, p. 484 (1929).

[†] 'Z. Physik,' vol. 78, p. 586 (1932).

There are also a considerable number of methods of determining transition probabilities by anomalous dispersion and similar methods,* which give τ in certain cases. In particular Ladenburg† measured the transition probabilities for a large number of neon lines, but it is only for the state $3\,^3D_3$, *i.e.*, the line $\lambda\,6402$, that sufficient data are available to calculate τ. For this state Ladenburg gives for τ an approximate value of $2 \cdot 5\,.\,10^{-8}$ seconds.

The Method.

The optical arrangement for the visual method of observation is shown in fig. 1.

T is the discharge tube of spectroscopic type filled with neon. The light emitted passes to the constant deviation spectroscope either directly or by reflection from the mirror M. KC is a Kerr cell filled with nitrobenzene, the potential on which is provided by an oscillator which also provides the potential for the discharge tube. The first Nicol prism N_1 is set with its axis at 45° to the lines of force in KC, the calcite crystal K is set with one of its images polarized parallel to the axis of N_1, and the second Nicol N_2 can be rotated. Observation consists in making the two images produced by the calcite crystal K of equal intensity by rotating N_2. In effect the Kerr cell system acts as a light shutter, and the angle δ through which the Nicol N_2 is rotated from the crossed position in order to make the two images of equal intensity gives a measure of the amount of light emerging from the system.

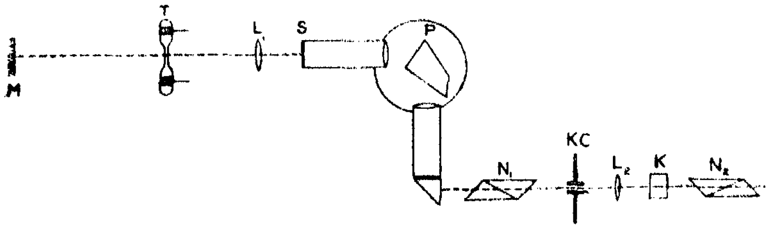

FIG. 1.

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* Korff and Breit, 'Rev. Mod. Phys.,' vol. 4, p. 471 (1932).

† Ladenburg and Minkowsky, 'Z. Physik,' vol. 6, p. 153 (1921); vol. 36, p. 839 (1926); 'Ann. Physik,' vol. 87, p. 296 (1928).

The experiment consists in changing the moment during the cycle at which the maximum of light reaches the Kerr cell. This can be done either by delaying the light by reflection over a long light path or by the introduction of a known electrical phase difference between the potential on the discharge tube and the potential on the Kerr cell. A curve may then be drawn between the effective phase difference introduced and the effect produced, *i.e.*, the angle δ. The position of the maximum or minimum of this curve gives sufficient data for the determination of the average life of the state τ when the original phase relations between the current in the discharge tube and the e.m.f. on the Kerr cell are known.

For later measurements a photographic method of observation was used. Here the light passes first to the Nicol N_1 and the Kerr cell and then to the spectrograph, in the collimator of which are the calcite crystal and second Nicol. The crystal makes two images of the slit and hence there are two spectra. Several exposures (usually 6) are made on the same plate with the Nicol N_2 moved (say) 2° each exposure. The densities of the lines are then measured on a Dobson photoelectric photometer, and the angle at which the images are of equal intensity found by interpolation.

By this method weaker lines may be measured, a permanent record is obtained and greater accuracy results. Factors such as the characteristic of the plate or the time of development, etc., do not affect the result, since it is only required to find the point at which the images are of equal intensity.

The Kerr Cell.

The theory and practice of the Kerr cell are becoming increasingly well known,* and it is only necessary to mention one or two points.

The cell was filled with nitrobenzene, which has by far the highest Kerr constant, but extreme care must be taken during its preparation to obtain the highest purity possible. The nitrobenzene used was prepared from benzene freed from thiophene, and after several distillations was treated with aluminium oxide, and purified by freezing and distillation *in vacuo*, the final distillation being into the Kerr cell, which could then be sealed off *in vacuo.*

The cell itself had electrodes of nickel 5 × 2 mm. sealed into a pyrex vessel. During construction the electrodes were separated by an aluminium spacer 0·2 mm. thick and bound together by aluminium wire, the aluminium being afterwards dissolved in caustic soda. Cells prepared in this way seemed to last almost indefinitely and the liquid was sufficiently pure not to cause distortion of the field when an H.F. potential was applied. Also it was not found necessary to superpose a constant on the H.F. potential to keep the field clear.

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* Beams, 'Rev. Mod. Phys.,' vol. 4, p. 133 (1932); 'Rev. Sci. Inst.,' vol. 1, p. 780 (1930).

It is necessary to consider here the possibility of a lag in the Kerr effect. Theoretically this should be below the limit of accuracy of the experiment, *i.e.*, of the order of 10^{-10} seconds.* A considerable amount of work has been done on the subject, but although some workers have apparently found a small lag, it has usually been shown later to be due to other causes. Lags have been found in liquids with large molecules and high viscosity, but there seems to be no evidence of a lag in nitrobenzene sufficiently large to affect this experiment. The effect of a lag in the Kerr cell would be to diminish the measured value of the lag in the emission of light. Hence results given in this paper should be increased by the amount of the lag in the Kerr effect.

If light passing through the cell is initially polarized at an angle of 45° to the lines of electric force, the intensities of the components of light emerging from the cell polarized parallel to and perpendicular to the incident light are proportional to

$$\cos^2 \mathrm{D}/_2 \quad \text{and} \quad \sin^2 \mathrm{D}/_2 \quad .$$

respectively, where $\mathrm{D} = 2\pi l \mathrm{BE}^2$.

Here B is the Kerr constant for the liquid, l is the length of path in the field, and E the field strength. The crystal separates the light into these two components and if the Nicol N_2 is now rotated through an angle δ from the crossed position to make the two images of equal intensity, we have

$$\sin^2 \delta \int_0^{\pi/p} \mathrm{I} \cos^2 \mathrm{D}/_2 \, dt = \cos^2 \delta \int_0^{\pi/p} \mathrm{I} \sin^2 \mathrm{D}/_2 \, dt,$$

since both I and E may not be constant in time.

Put $\mathrm{E} = \mathrm{E}_0 \sin pt$

then

$$\tan^2 \delta = \frac{\int_0^{\pi/p} \sin^2 (\pi l \mathrm{BE}_0{}^2 \sin^2 pt) \,.\, \mathrm{I} \,.\, dt}{\int_0^{\pi/p} \cos^2 (\pi l \mathrm{BE}_0{}^2 \sin^2 pt) \,.\, \mathrm{I} \,.\, dt},$$

which reduces to,

$$\cos 2\delta = \frac{\int_0^{\pi/p} \sin (\pi l \mathrm{BE}_0{}^2 \cos 2pt) \,.\, \mathrm{I} \,.\, dt}{\int_0^{\pi/p} \mathrm{I} \,.\, dt}. \qquad (1)$$

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* Debye, 'Marx Handbuch der Radiologie,' p. 661 (1925).

The Kerr cell was always operated under the conditions

$$\pi l B E_0^2 = \pi/2$$

the correct value of E_0 being found by using steady light, in which case δ first becomes 45° when $\pi l B E_0^2$ becomes $= \pi/2$. Actually the current through the cell was measured by a vacuum heater and thermojunction and the cell was calibrated for every frequency used.

Experimental.

(*a*) *Methods of producing any required Phase Difference.*—The most direct and usually the best method of changing the relative phase between the light entering the Kerr cell and potential on it is to send the light over a light path, the length of which can be varied at will. This is excellent for short wave-lengths of the oscillator, but becomes cumbersome for wave-lengths over 150 metres or so. For obtaining fairly quick readings of the difference in lag between different lines, the electrical arrangement described below was found to give good and consistent results.

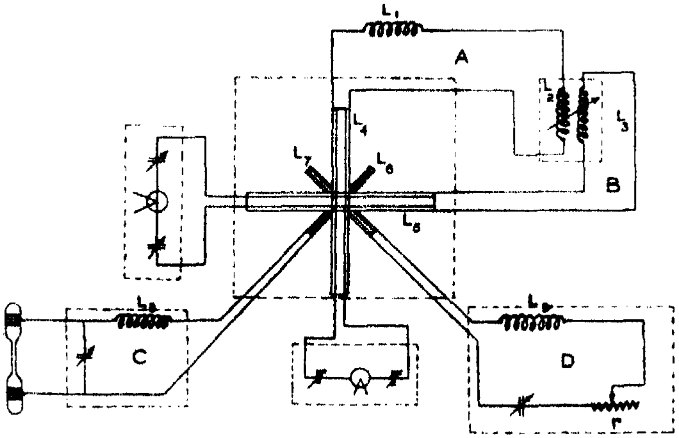

FIG. 2.

The circuit is shown in fig. 2. There are four separate circuits. Circuit A picks up energy from the oscillator by means of the unscreened coil L_1. B is inductively coupled to A by L_2L_3. L_4 and L_5 are square coils placed at right angles to each other. L_6 and L_7 are also at right angles to each other and can be rotated so that the common axis of L_6 and L_7 coincides with that of L_4 and L_5. All the circuits are tuned to the frequency of the oscillator and the coupling L_2L_3 is adjusted to make the currents in A and B of equal amplitude. Then since these currents differ in phase by 90° the phase of the potential on the discharge tube T differs from that of the current in A by approximately the angle between L_4 and L_6. It can be shown that if the maximum coupling between L_4 and L_6 is kept small, this relation is very well obeyed. In the actual apparatus used the error in phase was never more than 1·7°. The Kerr cell is connected to the anode coil of the oscillator. A number of measurements of the difference in lag of the different lines in the neon spectrum were made by this method, but, as will be seen later, the absolute value of the lag cannot be found by this method. Fig. 3 shows curves for the lines λ 6096 and λ 5853 obtained by this method. The difference between the lines is 10°, but the absolute value of α at the minimum is arbitrary.

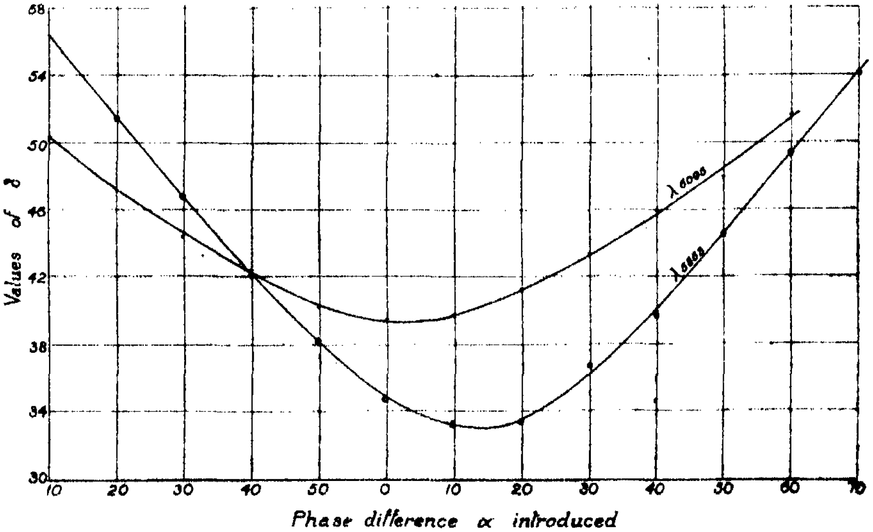

FIG. 3.

The circuit D is introduced for symmetry and the current in it is adjusted to the same amplitude as that in C.

(*b*) *Electrical Arrangements.*—The arrangements finally adopted to find the absolute lag is shown in fig. 4. The essential point of this arrangement is that the discharge tube T and Kerr cell KC are in series. In arrangements such as the electrical phase changer described above, the phase difference between the potential on the discharge tube and that on the Kerr cell is known, but the excitation depends on the current, *i.e.*, the number and speed of the electrons; thus the unknown phase difference between the potential on the discharge tube and the current through it is introduced. In the arrangement *shown in fig. 3 the current through the discharge tube will be exactly 90° out of phase with the voltage on the Kerr cell, since the latter is a pure capacity (the resistance of the cell was between* 10^7 *and* 10^8 *ohms).*

Measurements were made with this arrangement using the variable light path method and the results recorded photographically.

The coil L is of such an inductance as to form with the capacity of the Kerr cell a series resonant circuit of low impedance. Thus the lower electrode of the discharge tube will be almost at earth potential and also only the potential necessary to drive sufficient current through the discharge tube to work the Kerr cell, need be provided by the oscillator.

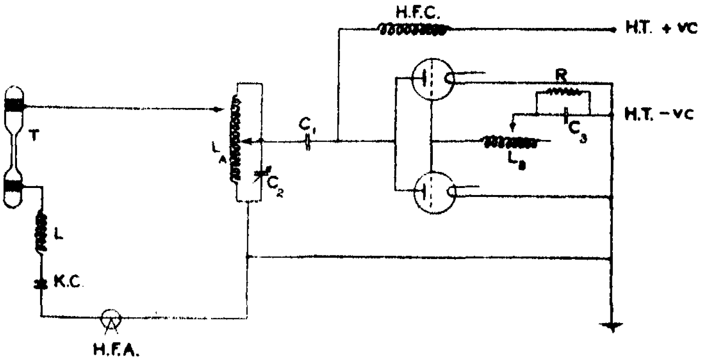

FIG. 4.

(*c*) In order to test the phase relations in this arrangement, a cathode ray oscillograph was used. One pair of deflector plates was connected to a toroidal coil placed round the centre part of the discharge tube and very carefully screened from electrostatic pick-up. The centre point of the coil was connected to earth. Two condensers were placed in series across the Kerr cell, one variable of about 5 cm. capacity and the other of 100 cm. The second pair of deflector plates was connected across the larger capacity, care had to be taken that the resonance frequency of the pick-up coil and its circuit did not occur near the frequency used. The resulting figure produced by the oscillograph was a straight line. This confirmed the above phase relations. The error was not greater than 1·2° phase difference.

This arrangement was also used to estimate the strength of the harmonics in the current through the discharge tube. An upper limit for this could be found, that for the 2nd harmonic being 1/5th of the fundamental and that for the 3rd harmonic 1/12th.

Theoretical Relation between the Observed Lag and the Average Life of a State.

It has been shown how a graph may be drawn of the relation between the observed angle δ and the phase difference γ introduced. From this may be found the position of the maximum or minimum. This we shall call the lag α. We must now determine theoretically how this lag depends on the average life of the state concerned.

If at any moment there are n atoms in a particular state, the rate at which n decreases owing to radiation is proportional to n and if there were n_0 atoms in this state at time $t = 0$ the number at time t is

$$n = n_0 e^{-\kappa t},$$

the average life is then $\tau = 1/\kappa$.

If this state is also being produced at a rate of $f(pt)$, we have

$$dn/dt = -\kappa n + f(pt),$$

putting $pt = \theta$ and $k = 1/p\tau = \kappa/p$,

$$dn/d\theta + kn = pf(\theta), \tag{2}$$

$f(\theta)$ is a function of the current and is periodic with a frequency twice that of the oscillator.

We now make an assumption with regard to $f(\theta)$, the validity of which will be examined later; namely, that the rate of excitation can be represented by a function $f(\theta)$ which is symmetrical about its maximum and is in phase with the current.

With this assumption $f(\theta)$ can be represented quite generally as a Fourier series of the type

$$f(\theta) = a_0 + \sum_{m=1}^{\infty} a_m \cos 2m\theta. \tag{3}$$

We can now find the Particular Integral of (2). The complementary function vanishes when t and therefore θ become large.

The solution is

$$n = \frac{a_0}{k} + \sum_{m=1}^{\infty} a_m \frac{2m \sin 2m\theta + k \cos 2m\theta}{(4m^2 + k^2)}. \tag{4}$$

This gives the number of atoms in the state at any moment and since the rate at which they emit light is proportional to n this also gives the form of the light curve.

This must now be substituted in the Kerr cell equation (1) for I with the phase difference γ introduced. This is the phase difference which is introduced experimentally by delaying the light or by the electrical phase changer.

The Kerr cell is operated under the condition $\pi l \mathrm{BE}_0^2 = \pi/2$, putting also $pt = \theta$ equation (1) becomes

$$\cos 2\delta = \frac{\int_0^\pi \sin(\pi/2 \cos 2\theta) \,.\, \mathrm{I} d\theta}{\int_0^\pi \mathrm{I} \,.\, d\theta}. \tag{5}$$

The denominator is the integral of (4) with $(\theta + \gamma)$ replacing θ.
This is

$$= \frac{a_0 \pi}{k} \tag{6}$$

$\sin(\pi/2 \cos 2\theta)$ can be expressed as a series of cosines with Bessel functions as coefficients, *i.e.*,

$$\sin(\pi/2 \cos 2\theta) = 2 \sum_{n=0}^{\infty} (-1)^n \mathrm{J}_{2n+1}(\pi/2) \cos 2(2n+1)\theta.$$

We therefore have to find the value of

$$\int_0^\pi 2 \sum_{n=0}^{\infty} (-1)^n \mathrm{J}_{2n+1}(\pi/2) \cos 2(2n+1)\theta$$
$$\times \left[\frac{a_0}{k} + \sum_{m=1}^{\infty} a_m \frac{2m \sin 2m(\theta+\gamma) + k \cos 2m(\theta+\gamma)}{(4m^2+k^2)}\right] d\theta.$$

On integrating, only terms involving $\cos^2 2(2n+1)\theta$ remain. The coefficient of $\cos 2m\theta$ in the second sum is

$$a_m \frac{2m \sin 2m\gamma + k \cos 2m\gamma}{(4m^2+k^2)}.$$

The value of

$$\int_0^\pi \cos^2 2(2n+1)\theta = \pi/2$$

and the integral becomes putting $m = 2n+1$

$$\pi \sum_{n=0}^{\infty} (-1)^n \mathrm{J}_{2n+1}(\pi/2)\, a_{2n+1} \frac{(2(2n+1) \sin 2(2n+1)\gamma + k \cos 2(2n+1)\gamma)}{4(2n+1)^2 + k^2}. \tag{7}$$

Finally from (5), (6), and (7) we obtain :—

$$\cos 2\delta = \frac{k}{a_0} \sum_{n=0}^{\infty} (-1)^n J_{2n+1}(\pi/2)\, a_{2n+1} \frac{(2(2n+1)\sin 2(2n+1)\gamma + k\cos 2(2n+1)\gamma)}{4(2n+1)^2 + k^2}. \tag{8}$$

We now require to find the maximum and minimum of δ.

Differentiating $w.r.t.\ \gamma$ and equating to zero we have

$$\sum_{n=0}^{\infty} (-1)^n \frac{J_{2n+1}(\pi/2)\, a_{2n+1}\, 2(2n+1)}{4(2n+1)^2 + k^2} \times \{2(2n+1)\cos 2(2n+1)\gamma - k \sin 2(2n+1)\gamma\} = 0. \tag{9}$$

This gives a relation between k and the values of γ for which δ is a maximum or minimum.

There are two main points to be noticed in this : First, that equation (9) gives values of γ between 0 and 45° as k goes from ∞ to 0 or as $p\tau$ goes from 0 to ∞. No lags greater than 45° should be observed.

Secondly, it will be noticed that the even harmonic terms have disappeared. Also the constants in the expansion decrease very rapidly and if a_3 is considerably smaller than a_1 as it is almost certain to be, the effect of the 3rd harmonic term becomes very small.

Taking the 1st term only (9) becomes

$$2\cos 2\gamma - k\sin 2\gamma = 0$$

or

$$\tan 2\gamma = 2/k = 2p\tau. \tag{10}$$

If the second term is included, the value of γ for a given value of k is slightly greater. The difference is zero at $\gamma = 0$ and 45° and is a maximum at about $\gamma = 22{\cdot}5°$. Thus when a_3/a_1 is 3/35 the maximum error in taking equation (10) is $0{\cdot}4°$ while when a_3/a_1 is 3/11 it is $1{\cdot}2°$.

Since there is no evidence as to the size of a_3 in the actual excitation curve, and the error is small, equation (10) is always used.

Comparison with Experiment.

It appeared from (10) that it would be impossible to obtain lags greater than 45°. The actual experimental results for a discharge tube of internal diameter 0·7 cm. gave lags up to 56°.

It was found empirically that if allowance were made for a displacement of the curve by a time τ', this time being the same for all frequencies, the resulting lags agreed with equation (10).

Allowing for τ' (10) becomes

$$\tan 2(\gamma - p\tau') = 2p\tau. \tag{11}$$

The best value of τ' was found to be $1\cdot6 \,.\, 10^{-8}$ seconds, while τ for λ 5853 is $3\cdot9 \,.\, 10^{-8}$ seconds.

Let us now examine the assumption made at the beginning of the previous section. We have seen that the harmonic terms produce a very small effect, thus the time, which we shall call the "extra lag," must be due to a difference of phase between the current and excitation, in such a way that the maximum of excitation occurs after the maximum of current. This can obviously be present when the electrons take a small but measurable time to disappear, for then a "building up" effect can take place so that the number of electrons increases after the maximum of current is passed.

With a view to testing this hypothesis experiments were performed with a discharge tube of internal diameter 1 mm. In such a tube the electrons should disappear more quickly and the lag decrease.

Curves were taken for the line λ 5853 at 150 metres and 2 mm. pressure, and the value of τ obtained from them by equation (10) agreed with that obtained with the larger tube using equation (11). Thus the "extra lag" had disappeared.

A different arrangement was also used with the narrower tube. Here the discharge tube was connected to a secondary tuned circuit, and the Kerr cell direct to the oscillator. The oscillograph was used to show when the current through the tube was in phase with that through the Kerr cell and the variable light path method was used. The results were again in agreement with those previously obtained.

The Effect of Pressure.

In the table of results the pressure of neon at which the readings were made is also given. It will be seen that within the range of pressure used, the value of the lag is independent of the pressure. Also it was found that within this range, the modulation of the light is independent of the pressure. To investigate the effect further, photographs were taken at selected points over a wide range of pressures, with the second Nicol set at the angle δ which had been previously obtained for this point. The results obtained can be summarized as follows :—

With the wider tube ($>$ 7 mm. diameter) above a pressure of about $0\cdot8$ mm. of Hg the light had very little modulation. From the lowest workable pressure

0·05 mm. to about 0·7 mm. no change was observed in the position of the maximum, and, moreover, the modulation remained the same.

With the narrow tube (1 mm. diameter) the modulation remained high up to larger pressures, *i.e.*, between 7 and 8 mm. of Hg. The limiting pressures are thus roughly in inverse ratio of the diameter of the tubes. Below the limiting pressure the modulation is higher than in the wider tube.

Most experiments on high frequency discharges in gases have been performed with fairly wide tubes, *i.e.*, 2 cm. diameter and upwards. With such tubes the limiting pressure would be low and the modulations very small. There is good evidence that the electrons disappear by diffusion to the walls and that recombination takes place on the walls and not in the centre of the discharge. It seems, then, that for the modulation to be high, the conditions must be such that the electrons may escape to the walls without many collisions and in a short time. The number of electrons present then changes considerably during the cycle. This agrees with the values of the limiting pressures, which give a kinetic theory value for the mean free path of electrons, of the same order as the radius of the discharge tube. Again the empirical value found for τ' is $1\cdot6 \,.\, 10^{-8}$ in a tube of diameter 7 mm. This would give to the electrons an average energy of $\frac{1}{2}$ volt in excess of that necessary just to reach the walls.

Below the limiting pressure the time that the electrons take to get to the walls produces the "extra lag," but also, the longer this time is, the less will be the modulation of the light. This is also in agreement with the experimental facts. It seems, then, that the excitation depends mainly on the number of electrons present, whereas the current also depends on their average velocity in the direction of the field.

From equation (8) an idea of the dependence of excitation on current can be obtained. Experimentally the limit to which δ maximum tends as $k \rightarrow \infty$ can be estimated, then neglecting higher terms than the first, the value of the ratio a_1/a_0 may be obtained from equation (8). This is found to be about 4/3. This is the same ratio as in $\cos^4 \theta$ which is

$$3/8\ (1 + 4/3 \cos 2\theta + 2/12 \cos 4\theta).$$

This gives an idea of the extent to which the excitation curve is peaked.

The modulation is also largely affected by the value of $p\tau$. Thus when $p\tau$ is large the modulation is small. Under the same conditions of pressure, and at the same frequency, this gives a further check on the relative values of τ for different lines. The correct order is found in all cases.

Table of Results.

For reference the main energy levels of neon are shown in fig. 5. The majority of the strong lines in the neon spectrum are formed by transitions from the upper ten levels of quantum number 3 to the four levels of number 2. Transitions to the ground level give lines in the far ultra-violet.

Most of the strong lines of neon have only weak lines very close, which would not affect the results. Moreover, the neon lines are not complicated by hyperfine structure except that due to the difference in mass of the two isotopes. There is thus no uncertainty as to what state is being observed.

In the table α is the actual value of the lag observed in degrees. Where the measurement was made with the larger tube, β is given as $(\alpha - p\tau') = \beta$ the value of τ' being taken as $1 \cdot 6 \,.\, 10^{-8}$ seconds as found above. τ is then calculated from

$$\tan 2\beta = 2p\tau.$$

For the smaller tube, $\alpha = \beta$. These measurements are marked with an asterisk.

Where the lags relative to that of λ 5853 were measured with the electrical phase changer, the difference is given as $\Delta\alpha$. This is then added to the appropriate value of α for λ 5853 at that wave-length. The pressure in millimetres of Hg is also given. This was measured by a McLeod gauge.

The measurement of β is accurate to about 1°. This produces an error in τ at $\beta = 22 \cdot 5^\circ$ of 7% at $\beta = 30^\circ$ of 25% and at $\beta = 40^\circ$ of 45%. The values of τ obtained all agree within these limits of error.

Discussion of Results.

(*a*) *Further Considerations affecting the Apparent Life.*—Two factors which tend to prolong the apparent life of a state have, as yet, been omitted. These are repopulation from higher levels and absorption and re-emission of the light.

Both are very difficult to estimate. However, it is clear that excitation to the higher levels is not overwhelmingly great, and is probably less than that to the lower levels, since the majority of electrons are of relatively low velocity. Again repopulation will only produce a difference in the measured life, if the life of the upper state is almost the same as that of the state it feeds. Further, the number of atoms dropping to the measured state from higher levels would, at least, have to be comparable with the number directly excited, before the effect would become noticeable. Thus it is likely that repopulation only plays

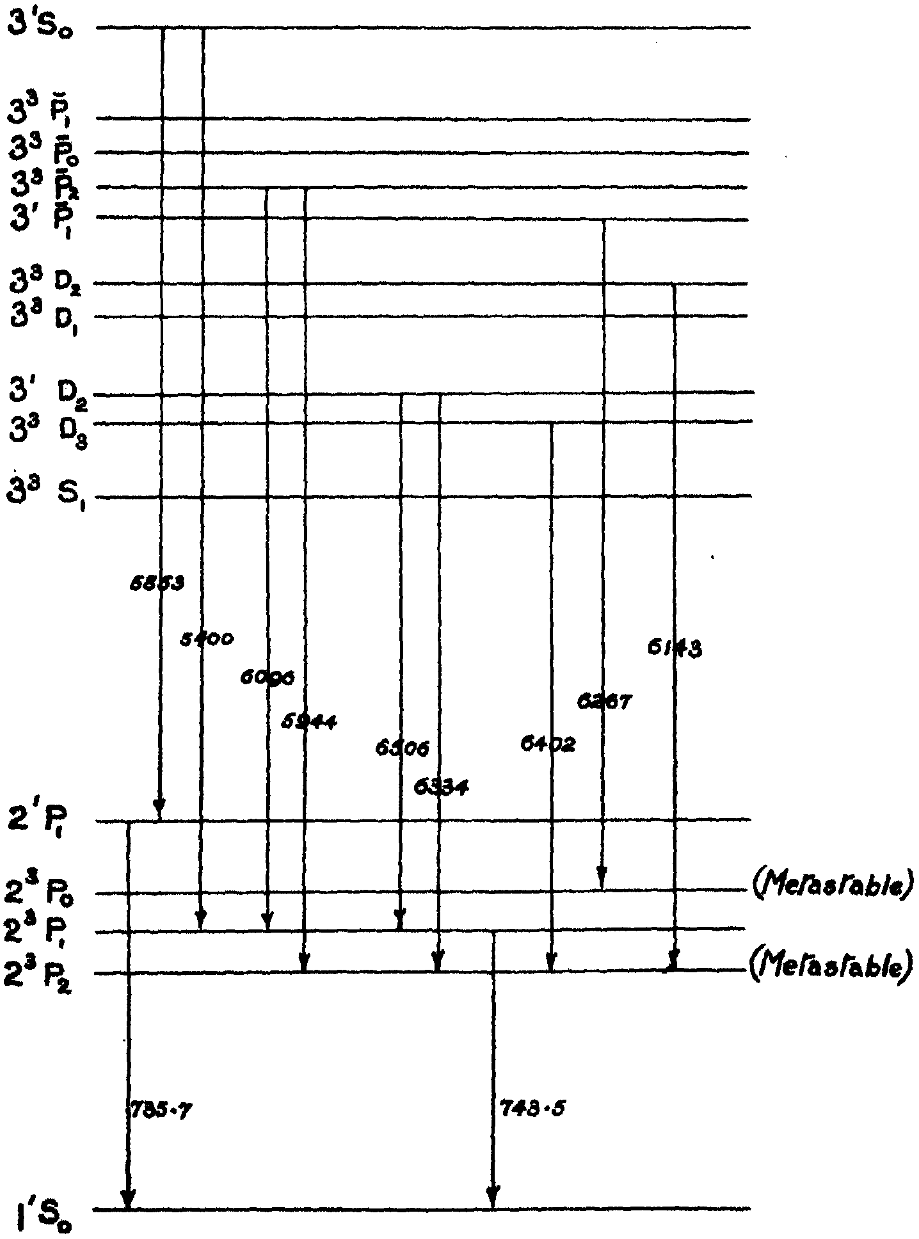
3^1S_0
$3^3\bar{P}_1$
$3^3\bar{P}_0$
$3^3\bar{P}_2$
$3^1\bar{P}_1$
3^3D_2
3^3D_1
3^1D_2
3^3D_3
3^3S_1
5853
5400
6096
5944
6506
6334
6402
6267
6143
2^1P_1
2^3P_0
2^3P_1
2^3P_2
(Metastable)
(Metastable)
735·7
743·5
1^1S_0

Fig. 5.

Table of Results.

Wave-length of line A.	Notation.	Wave-length of oscillation λ *el* metres.	Measured lag α°.	True lag $\beta^\circ = \alpha - p\tau'$.	Lag relative to λ 5853 $\Delta\alpha$.	β 5853.	Pressure in mm. of Hg.	$\tau \times 10^{-8}$ secs.	$\tau \times 10^{-8}$ average.
5853	$3\,{}^1S_0 \rightarrow 2\,{}^1P_1$	97	45·5	27·7	—	—	0·36	3·73	3·9 ± 0·15
		137	37·45	24·85	—	—	0·36	4·28	
		232	23·75	16·25	—	—	0·25	3·92	
		150	22·8	—	—	—	2·40	*4·05	
			20·9	—	—	—	0·33	*3·55	
			21·8	—	—	—	0·6	*3·78	
5400	$3\,{}^1S_0 \rightarrow 2\,{}^3P_1$	232	23·75	16·25	—	—	0·25	3·92	3·9 ± 0·15
5944	$3\,{}^3\overline{P}_2 \rightarrow 2\,{}^3P_2$	153	—	31·8	10	21·8	0·68	8·2	8·0 ± 1
6096	$3\,{}^3\overline{P}_2 \rightarrow 2\,{}^3P_1$	153	—	31·3	9·5	21·8	0·62	7·8	8·5 ± 1
		153	—	31·8	10	21·8	0·62	8·2	
		153	—	31·8	10	21·8	0·14	8·2	
		232	36·8	29·3	—	—	0·25	10·1	
6143	$3\,{}^3D_2 \rightarrow 2\,{}^3P_2$	153	—	32·8	11	21·8	0·62	9·0	9·0 ± 1
		153	—	33·8	12	21·8	0·62	9·8	
		153	—	31·8	10	21·8	0·14	8·2	
		232	36·5	29·0	—	—	0·25	9·8	
6267	$3\,{}^1\overline{P}_1 \rightarrow 2\,{}^3P_0$	127	—	36	11·5	24·5	0·27	10·4	11·5 ± 1·5
		153	—	35·8	14	21·8	0·62	12·2	
6334	$3\,{}^1D_2 \rightarrow 2\,{}^3P_2$	153	—	35·3	13·5	21·8	0·62	11·5	11·5 ± 1·5
6402	$3\,{}^3D_3 \rightarrow 2\,{}^3P_2$	127	—	40·5	16·0	24·5	0·27	21·3	20·0 ± 3
		153	—	39·3	17·5	21·8	0·62	20·2	
		153	—	37·8	16	21·8	0·14	15·9	
		232	44·7	37·2	—	—	0·25	22·0	
6506	$3\,{}^1D_2 \rightarrow 2\,{}^3P_1$	127	—	38·2	13·7	24·5	0·27	14·0	12·5 ± 1·5
		153	—	34·8	13	21·8	0·62	10·9	

a small part in this experiment, certainly much less than in Wien's method where most of the atoms start in ionized or highly excited states.

Absorption and re-emission will also lengthen the life of a state. Here only a small percentage of the light is absorbed and hence only a small percentage of atoms affected. Again most of the absorption will take place from metastable atoms of which there must be fewer than of normal atoms. Hence this again seems to be a factor which might influence the results by a small amount, but would not affect them seriously.

(*b*) *Lines originating from the same Upper Level.*—The value of τ for a given state should be the same whatever transition from that state is observed. For, although the transition probabilities may be different, this will only affect the relative intensities of the lines and not the value of τ which depends only on the sum of the probabilities.

Three cases of lines originating from the same upper level have been measured. The lines concerned are: λ 5853 A. and λ 5400 from the state $3\,{}^1S_0$; λ 6096 and λ 5944 from the state $3\,{}^3\overline{P}_2$; and λ 6506 and λ 6331 from the state $3\,{}^1P_2$. Of these the first pair gives the most striking proof of the above fact, since these have by far the shortest life observed. Measurements were made on λ 5400 with the electrical phase changer and gave a lag relative to that of λ 5853 of 1°, but the modulation was exactly the same. The line λ 5400 is very weak, but measurements were made of a few points at 232 metres with the variable light path method and these lay exactly on the curve for λ 5853 for that wave-length. It may be said, therefore, that these two lines have the same lag within the experimental error.

The other two pairs also agree with this conclusion, although here the lags are longer and therefore the measurements less accurate.

In conclusion, I should like to thank Professor Lindemann, both for his suggestion of the method and for his constant help and advice throughout the research.

Summary.

A method of measuring the average lives of the excited states of neon is described, in which a Kerr cell is used to find the lag between the emission of light and the current in a high-frequency discharge in neon. It is shown theoretically how this lag should depend on the average life of the state.

The results obtained agree with the theory if allowance is made for a small lag between the excitation and the current in the discharge tube. An explanation of this extra lag is given in terms of the motion of the electrons in the

discharge. Experiments with a narrower tube confirm this view, the extra lag becoming negligible.

The values of τ measured ranged from $3 \cdot 9 \,.\, 10^{-8}$ seconds for the line λ 5853 to $20 \,.\, 10^{-8}$ seconds for λ 6402, and it is shown that lines originating from the same upper level give the same value of τ.

The method possesses the following advantages :—

It may be used for any atom whose spectra can be produced in a high frequency discharge.

Sufficient light is produced to enable a spectrograph to be used. The quantity measured, *i.e.*, the lag, gives to a first approximation, the average life itself. Theoretical considerations can then be used to correct this value. The form of the excitation curve while having a small influence on the result does not produce a first order effect.

Measurements of the Relative Velocities of the α-Particles from Radon, Radium A, and Radium C′.

By G. H. BRIGGS, Ph.D., The University of Sydney.

(Communicated by Lord Rutherford, O.M., F.R.S.—Received October 3, 1933.)

[PLATE 4.]

In a previous paper* the writer described measurements of the velocities of the main groups of α-particles from thorium X and its four α-radiating products, relative to the radium C′ group which is commonly taken as a standard in such comparisons. The probable error in these measurements was estimated to be 1 in 20,000 to 1 in 30,000. Where comparable with the results published simultaneously by Rutherford, Wynn-Williams, Lewis, and Bowden,† the agreement is very satisfactory, namely, 1 in 10,000 for thorium C (mean) relative to radium C′ and 1 in 30,000 for thorium C′. The present paper describes experiments in which the relative velocities of the radon, radium A, and radium C′ groups have been measured, using apparatus of greater resolving power than in the experiments with thorium X ; the probable error of the results is estimated to be of the order of 1 in 80,000. According to these experiments the velocities of the radon and radium A groups are somewhat higher than found in recent experiments by other observers.

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* 'Proc. Roy. Soc.,' A, vol. 139, p. 638 (1933).

† *Ibid.*, vol. 139, p. 618 (1933).

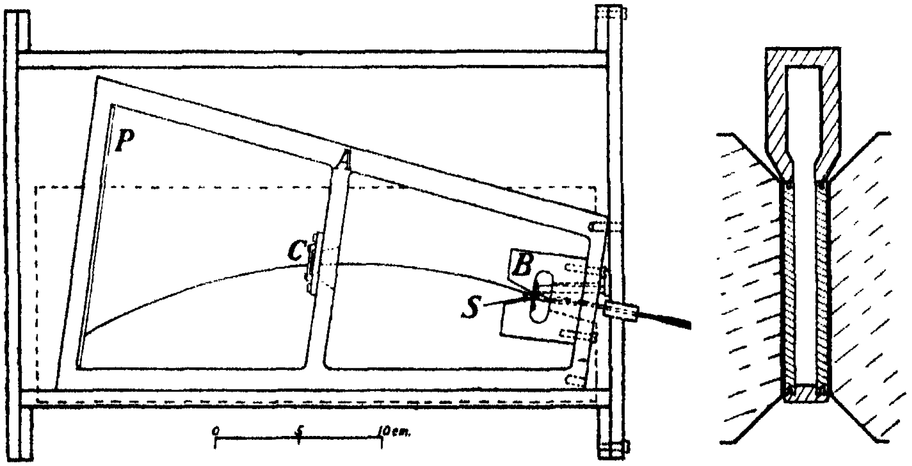
Experimental Method.

As in the experiments with thorium X the relative velocities were determined from the deflections recorded on a photographic plate using the earlier, or direct, magnetic deflection method. The source of α-particles was radon of high purity introduced directly from a purification plant into a small glass chamber which had a thin mica window and was situated within the vacuum exposure box. The correction for loss of velocity in the window was determined experimentally and the radon chamber was designed so that errors due to the recoil of the active deposit into the window or walls of the chamber would be eliminated.

The Deflection Apparatus.—The electromagnet was built from portions of an old-fashioned 2-pole dynamo kindly given by Professor J. P. V. Madsen, of the Department of Electrical Engineering of the University of Sydney. The field magnets and yoke were in one solid piece of U-form with a section 33 by 16 cm. Poles of overall dimensions 33 × 28·5 × 18 cm. were fitted giving a gap of area 33 × 13 cm. and of adjustable width. The whole of the magnet except the poles was immersed in a tank of oil which was cooled by water circulating in metal tubing wound over the magnetizing coils. With a current of 6·8 amperes and a gap of 1·3 cm. the field was about 10,500 gauss.

The experiments were made using the method of double deflections, *i.e.*, deflected lines were obtained on the plate on either side of the undeflected position. This method eliminates several sources of error which may arise if the deflections are in one direction only. The two deflections may be obtained either by reversing the field or by reversing the frame carrying the plate and slits. The latter method, which was used throughout this work, involves more manipulations particularly in the present experiments, but it has two very important advantages for the path of the particles may be arranged in the most uniform part of the field, and, if the field is strong enough to produce deflections comparable with the depth of the air gap, it is possible to arrange for a much larger double deflection than could be obtained by reversing the field.

To reduce the air gap the exposure box, shown in figs. 1 (*a*) and 1 (*b*), was built with sides of mild steel. The photographic plate P and the necessary slits were rigidly attached to a cast aluminium frame A, symmetrical about its longer axis. The slit S, 0·09 mm. wide, through which the α-particles enter from the radon chamber was made of hard gold and mounted on the axis of the frame on a brass block B, as shown in the diagram. The distance from this slit to the plate was approximately 26 cm. At C, midway between the slit S and the plate, were four slits 1 mm. apart and about 0·05 mm. wide.



(a) (b)

FIG. 1 (a).—The exposure box and frame carrying photographic plate and slits.
(b).—Section through poles and exposure box.

The Radon Apparatus.—A radon chamber is shown in detail in fig. 2 (a). These chambers were made by blowing a small thick walled bulb on the end of a pyrex capillary of about 2 mm. external diameter. This bulb was then flattened, the end ground off, and the interior shaped in a blowpipe until it was approximately rectangular, the opening being about 5 mm. by 1 mm. and the depth about 3 mm. The thickness of the mica windows ranged from about $1 \cdot 8 \times 10^{-4}$ to $2 \cdot 7 \times 10^{-4}$ mm., *i.e.*, from 0·4 to 0·6 mm. air equivalent. Thinner windows were impracticable owing to the difficulty of handling and danger of breaking. Areas of suitable and uniform thickness could be readily recognized from the brilliant interference colours shown. To conform with the precision of the other measurements in the experiments it was necessary to know the mass per unit area of the mica to about 1%. This was found by weighing the pieces on a quartz fibre flexure micro-balance similar in principle to that described by Bazzoni,* and measuring their area on a fine photographic grid having 12·5 squares per square millimetre. The mica was cemented to the pyrex chambers with "Collins Elastic Glue," a wax somewhat like picein. All traces of grit were first removed from the wax by dissolving in ether and filtering ; the ether was then driven off by prolonged heating.

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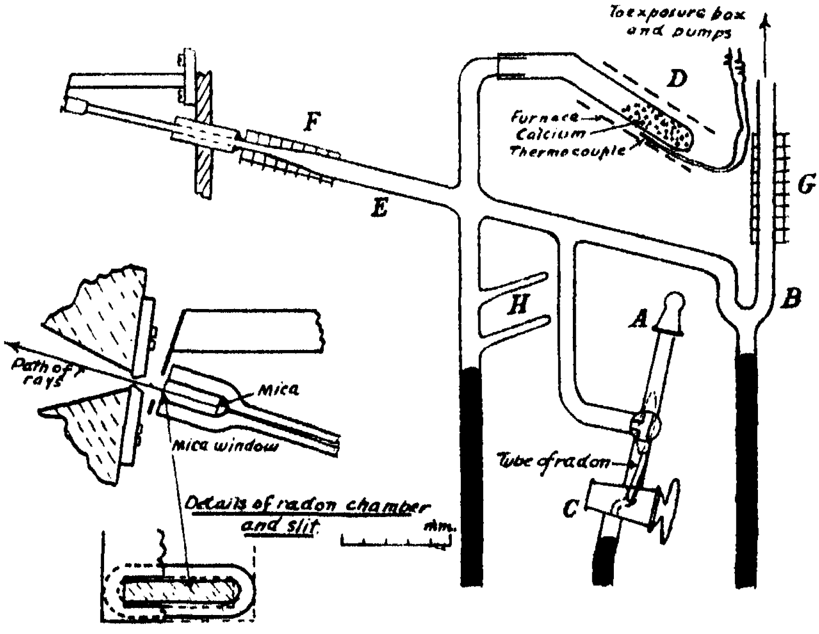
* 'J. Opt. Soc. Amer.,' vol. 9, p. 685 (1924).

As the amount of emanation in the chamber might be as much as 100 to 150 millicuries the heat produced in the disintegration had to be considered. Rough calculations showed that the temperature of the chamber would rise initially at about 20° C. per minute. To reduce this effect and to prevent the wax softening strips of copper were therefore waxed to the two flat sides of the chamber and joined to the end plate of the box. In later experiments the cooling was improved by waxing a very close fitting copper cradle around the chamber.



(*a*) (*b*)

FIG. 2 (*a*).—The radon chamber ; (*b*) the radon purification apparatus.

The radon purifying apparatus is shown in fig. 2 (*b*). It was designed so that comparatively large quantities of radon of a high degree of purity could be introduced into the chamber, the pressure could be determined, repurification could be carried out during the course of an experiment if necessary, the radon could be stored away when air had to be admitted to the exposure box, and so that in the course of the evacuation of the exposure box and radon apparatus the pressure difference on the two sides of the window would not at any time exceed 1 or 2 cm. of mercury.

The capillary tube containing the radon was introduced at A. The purifying apparatus and the exposure box were pumped out simultaneously and the radon apparatus was then cut off from the box and pumping system by the mercury cut-off B. The radon capillary was broken by the tap C and the radon forced up into contact with the purifying agent, calcium, heated to about 730° C. in the quartz tube D. After purification the radon was collected with liquid air at E and then pushed over mercury towards the radon chamber. The pressure of the radon was determined from the readings of the mercury on the scales at F and G, the apparatus having been previously calibrated with the radon chamber completely evacuated. This pressure was generally 3 to 6 mm., about half of which was due to the partial pressure of the radon. In order to allow radium C to accumulate and so obtain lines of more nearly equal intensity, and also to avoid error due to the combined effect of lack of equilibrium between the three products and possible variation of the field during the experiment, the exposure was not commenced until the radon had been in the chamber at least an hour. The length of exposure for the lines deflected in one direction was from 2½ to 4 hours according to the amount of radon. At the end of this exposure the radon was condensed in the side tubes H, air admitted, the frame carrying the plate and slits turned upside down, and after repurifying the radon a second exposure was made to obtain lines deflected towards the other end of the plate. In some experiments the magnet was demagnetized at a convenient stage and an exposure of about 10 minutes given to obtain undeflected lines.

Excellent photographs with hardly any trace of background fog were obtained with Ilford Process plates; the double deflections for the radium C′, radium A, and radon groups were about 9·8, 11·4, and 12·1 cm. Typical photographs are shown in Plate 4. The deflections were determined as in the previous work from the density curves obtained with a microphotometer having an accurately calibrated screw with a travel of 17 cm. The centre of a line could be determined to 0·0003 mm. and errors in the measurements of the deflections were negligible in comparison with other errors. Typical photometer curves are shown in fig. 3.

To reduce the amount of calculation in the determination of the radii of curvature the general procedure was to apply corrections to reduce the observed double deflections for the four slits to the values they would have for a slit on the normal from the source to the plate. These corrections could be accurately calculated from the geometry of the apparatus and the radii of curvature of the paths of the three groups. The deflections in the two directions may not be exactly equal owing to the field being slightly different in the two exposures, but it was verified that no error will arise in taking the deflection as half the double deflection after correction for slit angle. A typical set of deflections, before and after correction for slit angle, together with the calculated velocity ratios are given in Table I.

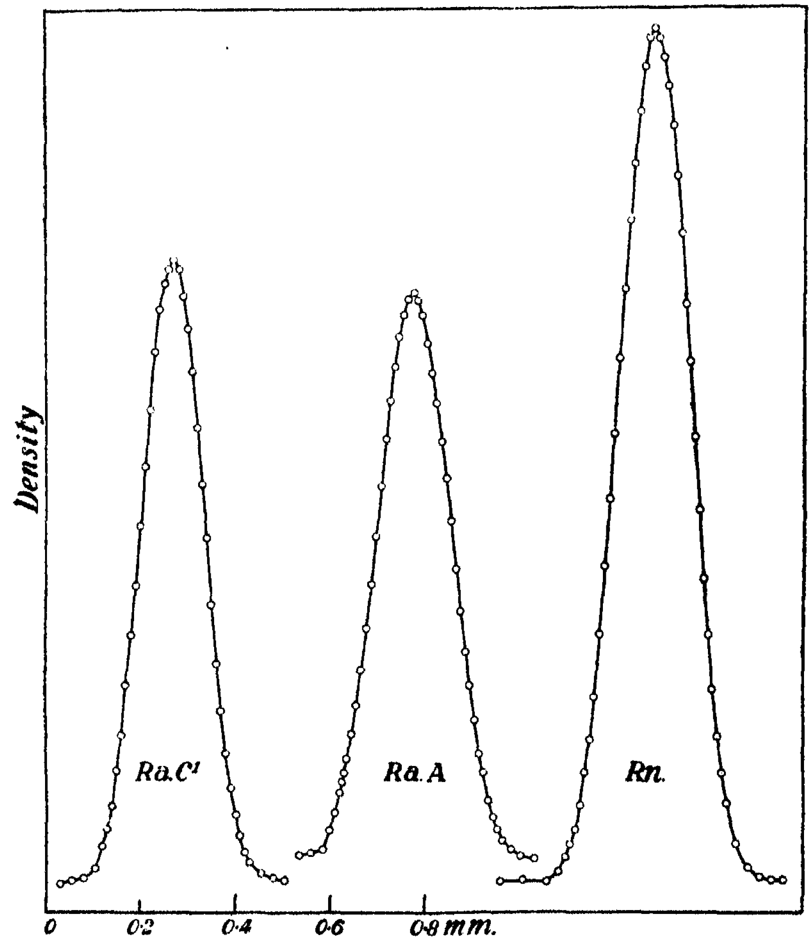


Fig. 3.—Typical density curves. Mica window 0·505 mm. air equivalent. Direction of deflection, left to right. The curves are displaced relative to one another for convenience of reproduction.

Table I.

Slit No.	Double deflections (mm.).						Observed velocity relative to radium C′.	
	Radium C′.		Radium A.		Radon.			
	Observed.	Corrected for slit angle.	Observed.	Corrected for slit angle.	Observed.	Corrected for slit angle.	Radium A.	Radon.
1	98·0160	97·9733	114·2030	114·1471	121·0088	120·9464	0·882694	0·843701
2	97·9813	97·9721	114·1537	114·1439	120·9394	120·9462	0·882704	0·843694
3	97·9721	97·9719	114·1449	114·1446	120·9487	120·9453	0·882699	0·843697
4	97·9580	97·9696	114·1633	114·1432	120·9713	120·9488	0·882689	0·843661
						Mean	0·882697	0·843688

Corrections and Sources of Error.

Since a high accuracy is claimed for the final results of these measurements it is important to describe in some detail the methods of determining the various corrections which have to be applied to the observed velocity ratios and to discuss possible sources of error.

(*a*) *Correction for the Mica Window.*—To determine accurately this correction, which may amount to as much as 1 in 500, a number of experiments were made in which a piece of mica about ten times as thick as the window was interposed between the window and the slit D, so that two-thirds of the rays traversed this additional sheet of mica and gave lines on the plate in addition to those due to rays which had traversed the window alone. Only two slits could be used in these experiments owing to the overlapping of some of the lines. One of the plates so obtained is shown in figs. 7 and 8, Plate 4.

Since the retardation produced varies rapidly with the initial velocity the correction for the window is not directly proportional to the retardation produced by the thicker mica. It is not imperative for the calculation of the required corrections to introduce the ranges of the α-particles but it is very convenient to do so. Writing

$$\left(\frac{V - \delta V}{V}\right)^p = \frac{R - \delta R}{R}, \tag{1}$$

where V and R, V — δV, and R — δR are the velocity and range before and after traversing the thicker mica, these experiments determine three values of

p, one for each group of α-particles. The correction for the mica window in the main experiment may then be calculated from the equation

$$\frac{V}{V_0} = \frac{V'}{V'_0}\frac{(1-[\delta R/R_0])^{1/p}}{(1-[\delta R/R])^{1/p}}, \tag{2}$$

where V/V_0 is the required velocity ratio, V'/V'_0 the observed velocity ratio and δR the air equivalent of the window. Since the ranges in air must be used for R_0 and R a conversion factor is required to calculate δR in equations (1) and (2). Assuming that mica of mass 1·43 mg. per sq. cm. is equivalent in stopping power to 1 cm. of air at 15° C. and 760 mm. pressure (and in these calculations this factor need be known only approximately) the mean values of p found in four experiments with different chambers, windows, and correction micas were 3·154, 3·090, and 3·072 for the initial velocities of the radium C′, radium A, and radon groups respectively, the error being not more than 1 in 300. These values decrease with velocity in much the same way as the values for air found in the author's work on the velocities of the α-particles from thorium X, but they are consistently smaller, indicating that the conversion factor for mica assumed above is too high. This discrepancy, or the assumption of a conversion factor constant along the range, does not invalidate the method of calculating the corrections, since changes in the conversion factor of as much as 10% produce compensating changes in the values of p which leave the calculated corrections unaltered. These corrections to the velocity ratios are of the order of 1 in 500 and the maximum error in an experiment due to their uncertainty is about 1 in 70,000, the greater part of which is an accidental and not a systematic error. The corrections are given in Table II.

(*b*) *The Magnetic Field.*—No direct measurements of the constancy of the field during an exposure were made. To avoid variation of the field due to temperature changes the magnet was warmed up before commencing an exposure and then maintained at a fairly constant temperature by the cooling system. Also, in setting the current the magnet was brought into a steady magnetic state by raising and lowering the current in a series of decreasing steps above and below the final current required. There is very good evidence from the uniformity of the widths of corresponding lines in different experiments that any variation in the field was small. Such variation only produces error in the results owing to the lack of equilibrium, in the early part of the exposure, between the radium C′ and the radon. The period of 1 hour or more allowed for the growth of RaC′ before starting reduces the maximum error to the order of one-thirtieth of the maximum field variation, and the net effect must be small compared with other errors.

The magnetic field was explored for inhomogeneity on three occasions during the experiments, using a small search coil and ballistic galvanometer having a sensitivity of 1·70 gauss per centimetre throw. The exploration was carried out in two stages. Variations were first measured along a series of lines perpendicular to the paths of the particles and then along a horizontal line cutting the paths. From these the variations along the paths of the three groups which pass through the central slit were determined. As the deflections of the particles cannot be treated as small, Hartree's method* was applied to each of these paths to calculate the effect of the field variations. The net correction was very small, namely, 3 ± 10 in 10^6 for the velocities of the radon and radium A groups relative to the radium C′ group. The small magnitude of the correction is partly fortuitous. It is readily shown that as a result of the reversal of the plate-carrier the corrections are the same for all four slits since the rate of variation of the field along a line normal to the path was nearly linear.

(*c*) *Correction for Absorption by Gas in the Chamber.*—The α-particles pass, on the average, through a thickness of gas equal to half the depth of the radon chamber. Generally the initial pressure of the gases was 3 to 6 mm. of which about half was due to the radon. The pressure was observed periodically during the exposure capillary effects being taken into account; it was invariably found to increase, the mercury retreating slightly in the tube connecting the radon chamber to the radon apparatus. It was assumed that the impurity initially present is carbon dioxide, as is indicated by Wertenstein's† experiments, and that the gas subsequently released has the same stopping power as air. If the total pressure became greater than 10 mm. the radon was re-purified without otherwise interrupting the experiment. The corrections to the velocity ratios for retardation by the gases are principally due to the radon, and as they are of the order of only 1 or 2 in 20,000 they can be calculated with sufficient accuracy with the above assumptions from the dimensions of the chamber and connecting tube, the amount of radon and the observations of the pressure. The error in a single experiment on account of uncertainty in this correction should not exceed 1 in 80,000 of which only part should be systematic.

(*d*) *Deposit on Mica Window.*—Although the source of α-particles was designed so that errors due to loss of velocity might be eliminated or be calculated exactly, this was not quite realized, for it was found that after use the mica windows showed, when examined with a powerful lens, a slight deposit on the inside which was detected by an irregular change in the interference colour of the window. This deposit was probably due to the action of the radiations on the small free area of the wax used for attaching the mica, but it was impracticable to use a more resistant material such as silver chloride. There was fairly definite evidence that the deposit was appreciably reduced when the cooling of the chamber was improved. While it was impossible to determine precisely the error introduced by this deposit in any one experiment, fairly consistent estimates of the general order of the effect were made both from the changes it produced in the interference colour of the various windows and also from the decrease in the velocity ratios in a series of five experiments with one window. In the latter case the effect was large enough to become measurable. There was definite evidence that the deposit increases, as might be expected, with exposure. The corrections are about 1 in 80,000 for a first experiment with a window, and, assuming that the increase with exposure is uniform, they will be three times as large in a second experiment. The actual corrections applied are given in Table II. They may be in error by as much as 50%. There was no evidence that the intense radiation had any harmful effect on the window, for the deposit could be driven off by heating leaving the original interference colour of the window unaltered.

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* 'Proc. Camb. Phil. Soc.,' vol. 21, p. 746 (1922–23).

† 'Phil. Mag.,' vol. 5, p. 1017 (1929).

The question whether this deposit, by the occlusion of radon, will prevent the effect of recoil into the window being completely eliminated by the equal recoil into the mica at the back of the chamber, has been carefully considered, and it is concluded that there is no evidence for appreciable occlusion, and even if 20% of the α-particles originated from radon thus occluded the effect on the relative velocities would be less than 3 in 10^6.

(*e*) *The Photographic Plates.*—(i) It is well known that movement of the photographic emulsion in the process of development or drying may be a source of error in measurements such as described in this paper. To reduce such movements the plates were developed at 12° C., fixed and washed at 5° C., and then dried uniformly. This was done by removing surplus moisture with a fine linen cloth and allowing the plates to dry in a horizontal position in a box in which the air was violently stirred. Tests made as described in a previous paper,* and capable of detecting movements of 0·001 mm. revealed no shifts at all, even within half a millimetre of the end of the plates. There should be no error therefore on this account.

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* Briggs, *loc. cit.*

Table II.

Air equivalent of mica.	Velocities relative to the radium C′ group.			
	Radium A.		Radon.	
	Observed velocity and (i) correction for window (ii) correction for gas in radon chamber (iii) correction for deposit on window.		Observed velocity and (i) correction for window (ii) correction for gas in radon chamber (iii) correction for deposit on window.	
mm.				
0·582	0·882749		0·843731	
	1239		1730	
	27		37	
	9		12	
		0·884024		0·845510
	0·882808		0·843779	
	1239		1730	
	22		31	
	26		36	
		0·884095		0·845576
0·586	0·882697		0·843688	
	1247		1742	
	53		73	
	9		12	
		0·884006		0·845515
	0·882691		0·843665	
	1247		1742	
	56		78	
	26		36	
		0·884020		0·845521
0·605	0·882694		0·843659	
	1288		1800	
	54		75	
	9		12	
		0·884045		0·845546
	0·882741		0·843692	
	1288		1800	
	56		78	
	26		36	
		0·884111		0·845606
0·505	0·882801		0·843812	
	1074		1499	
	79		108	
	14		20	
		0·883968		0·845439
	0·882842		0·843873	
	1074		1499	
	60		82	
	42		60	
		0·884018		0·845514
0·587	0·882719		0·843768	
	1250		1746	
	47		65	
	9		12	
		0·884025		0·845591
	0·882749		0·843775	
	1250		1746	
	39		54	
	26		36	
		0·884064		0·845611
Means		0·884030		0·845535

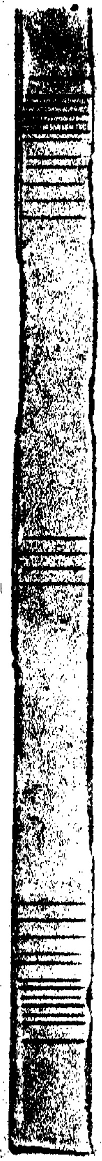

Fig. 4.

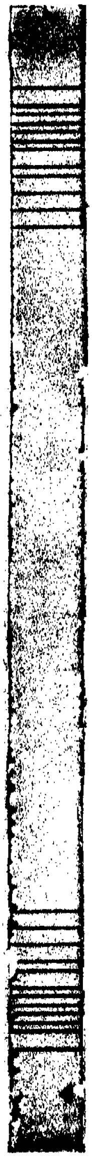

Fig. 5.

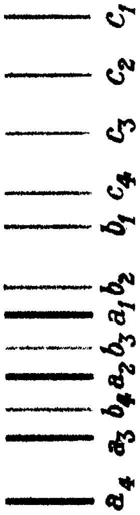

Fig. 6.

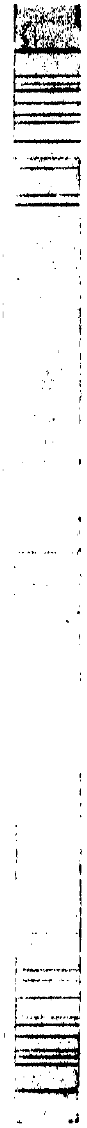

Fig. 7.

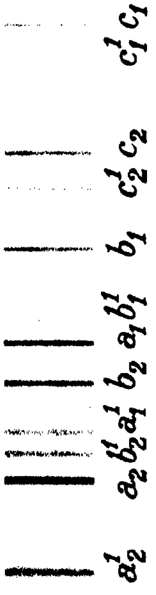

Fig. 8.

(*Facing p.* 614.)

(ii) The α-particles enter the emulsion of the plate at an angle of about 45°. The effect of this on the measured deflection is equivalent to that of a series of deflections differing slightly owing to change in the distance between source and film. The film thickness is so small that it can be readily shown that no correction on this account is necessary since only relative velocities are being measured.

The Results.

The final results are based on ten plates which were obtained in the first and second experiments with five different chambers and windows. Experiments beyond the second with any window are excluded owing to the uncertainty in the correction for the deposit on the window.

In Table II the observed velocity ratios are shown with the various corrections. For convenience the correction for inhomogeneity of the magnetic field, which is constant throughout, and the relativity corrections have been included in the tabulated results for the observed ratios. The result of a second experiment with a window appears in the table below that of the first experiment and has been given a weight a half that of the first. It is noticeable that all the second experiments give results slightly greater than the first. However, there is no evidence that this is really significant as among the preliminary experiments, which will be referred to below, the reverse sometimes occurred. The probable error calculated from the spread of the 10 pairs of results is only 6 or 7 in the sixth significant figure, but in estimating the precision of the final mean values the presence of systematic errors must be considered. The inhomogeneity of the field, the deposit on the window, the measurement of the distances from source to plate and slits, and to some extent the determination of the values of p for the mica correction introduce systematic errors. Taking these into account it is considered that the precision of the measurements may be expressed as a probable error of about 1 in 80,000.

The relative velocities determined in these experiments are summarized in Table III. The absolute velocities and energies have been calculated taking $1 \cdot 922 \times 10^9$ cm. per second and $7 \cdot 683 \times 10^6$ electron-volts as the velocity and energy of an α-particle from radium C′. Although the absolute velocity is only known to 1 in 2000, the figures in brackets have been included for the comparison of the ratios or the differences of these quantities.

In the preliminary experiments five plates were obtained which have not been included in the final results because it was considered that the experimental arrangements were not quite satisfactory; for example, in these experiments no interval for growth of radium C′ was allowed before starting, and one window

Table III.

	Relative velocity and probable error.	Velocity in cm. per sec. $\times 10^{-9}$.	Energy of α-particle in e. volts $\times 10^{-6}$.	Disintegration energy in e. volts $\times 10^{-6}$.
Radon	0·845535 ± 0·000010	1·625 (12)	5·487 (96)	5·588 (67)
Radium A ...	0·884030 ± 0·000011	1·699 (11)	6·000 (27)	6·112 (44)
Radium C′ ...	1·000000	1·922 (00)	7·683 (00)	7·829 (36)
Radon	0·956455 ± 0·000010			
Radium A	1·000000			

was comparatively thick, 0·886 mm. air equivalent. The results were not so consistent as in the later experiments, but the means agreed with the final results to 1 in 12,000.

Valuable evidence for the reliability of these measurements is furnished by the almost perfect symmetry of the density curves of the lines. In velocity measurements one of the most troublesome errors arises from the difficulty of preparing sources free from retarding effects. In direct deflection measurements such sources generally give rise to a tail on the low velocity side of the line. In the present experiments a low velocity tail was just detectable on most of the lines by careful measurement of the density curves. It was so small that at one-tenth of the height of the curves the mid-point of the width corresponded to a deflection which, averaged over a number of plates, was only 0·001 mm. more than the peak deflection, *i.e.*, an increase in deflection of about 1 in 50,000. On the curves for the best plates fairly precise measurements could be made even at one-hundredth of the total height and here the increase in deflection of the mid-point of the width was about 0·004 mm. for both the radium C′ and the radon lines. The effect could not be measured so precisely at this height on the less dense radium A lines, but it was not appreciably different. A definite increase in the tail was noticed in some experiments in which a window was used for the fourth and fifth times suggesting that in part at least it is due to the deposit on the inside of the mica window being somewhat irregular. Any retardation which the tail indicates has to this extent been included in the correction for the deposit. If, however, it is regarded as indicating an unknown source of error its magnitude can be estimated, from the author's investigation of a much larger effect of this kind in the work with thorium X, to be less than 1 in 150,000.

It appears from approximate calculations based on the width of the appreciably straggled groups which have passed through the correction micas that the observed width of the main lines, apart from the low velocity tail, can be completely accounted for by the straggling of the α-particles in the mica window and the gas in the chamber. From this and the small size of the low velocity tail, it can be concluded that any initial inhomogeneity in the velocities of the α-particles cannot be greater than 1 in 5000. This is of the same order as the upper limit to the inhomogeneity found by Rutherford and his collaborators.

The velocities for radium A and radon found here are both higher than those found by Rosenblum and Dupouy,* Rosenblum,† and by Rutherford, Wynn-Williams, Lewis, and Bowden (*loc. cit.*). For radium A the differences, which amount to 1 in 2000 from the value found by Rosenblum and Dupouy, and 1 in 3000 from that found by Rutherford and co-workers, are probably within the limit of their experimental errors. The velocities for radon relative to radium C′ were found both by Rosenblum and by Rutherford by comparison first with radium A. Here the discrepancies are greater, but taking into account the two steps in the comparison do not exceed their experimental errors.

I wish to express my thanks to the Trustees of the Commonwealth Science and Industry Endowment for assistance when the construction of the electromagnet was first undertaken. I am indebted to the Department of Cancer Research of the University of Sydney for the supplies of radon, and to the Commonwealth Oxygen Company for liquid air. I acknowledge gratefully the help of my wife in the photometering of the plates, and of my former assistant Mr. J. Thompson, in the course of the work.

Summary.

The relative velocities of the α-particles from radon, radium A, and radium C′ have been measured by the direct deflection method. The probable error in the measurement is estimated to be 1 in 80,000. The source of α-particles was radon of high purity and low pressure in a small glass chamber provided with a very thin mica window, the correction for which was determined experimentally.

DESCRIPTION OF PLATE.

FIGS. 4 and 5.—Typical plates obtained with four slit apparatus.

FIG. 6.—Left-hand group of 5 enlarged. a_1, a_2, a_3, a_4, radon lines from slits 1, 2, 3, and 4; b, radium A lines; c, radium C′ lines.

FIG. 7.—A plate used in determination of correction for mica window.

FIG. 8.—Left-hand group of 7 enlarged. The groups a, b, and c have passed through window alone. a', b', and c' have passed through mica of air equivalent 4·38 mm. in addition.

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* 'C. R. Acad. Sci. Paris,' vol. 194, p. 1919 (1932); 'J. Phys. Rad.,' vol. 4, p. 262 (1933).

† 'C. R. Acad. Sci. Paris,' vol. 195, p. 317 (1932).

Refractive Dispersion of Organic Compounds. Part IV.—*Cyclohexene and* 1 : 3-*Cyclohexadiene.*

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(Communicated by T. M. Lowry, F.R.S.—Received October 4, 1933.)

In the present paper the measurements of the refractive dispersion of *cyclo*hexane and benzene, described in Parts II and III of the present series,* have been supplemented by measurements of two intermediate hydrocarbons, namely, *cyclo*hexane and *cyclo*hexadiene. Data are therefore now available for the whole of the cyclic hydrocarbons of the series, C_6H_6, C_6H_8, C_6H_{10}, C_6H_{12}. It has, however, been possible to examine only one of the two isomeric forms of the hydrocarbon, C_6H_8, namely, the 1 : 3-diene, since the 1 : 4-diene has not yet been prepared sufficiently free from the 1 : 3-isomer to justify accurate physical measurements. The absorption spectra of the two unsaturated hydrocarbons have also been plotted and compared with those of benzene.

Materials.—(*a*) *Cyclohexene* was prepared by the method of Zelinsky and Zelikow.† Cyclohexanol (40 gm.) was heated at 100–110° C. under a reflux condenser for 24 hours with oxalic acid (200 gm.) previously dehydrated by heating at 120° C. for 12 hours in an air-oven. The cyclohexene was distilled from the solid mass and was fractionated over sodium. The fraction distilling at 83–84° was collected, kept over sodium, and refractionated immediately before use. The final product boiled at 83·1° C. and its density was $d_4^{20} = 0\cdot8110$, in agreement with the value 0·8111 interpolated from those given by Zelinski and Zelikow, $d_4^{27} = 0\cdot8054$, and by Auwers,‡ $d_4^{15\cdot1} = 0\cdot8147$, for specimens specially prepared for a similar purpose. Observations were also made with a sample of cyclohexene supplied by Dr. Waterman of Delft. The refractive indices of this sample were measured with an unmodified Pulfrich refractometer for 18 wave-lengths in the visible spectrum. The values thus obtained differ from those recorded for our own specimen by an average of only ±0·0001, which is of the same order as the accuracy obtainable with the instrument as then used.

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* Lowry and Allsopp, "Refractive Dispersion of Organic Compounds," 'Proc. Roy. Soc.,' A, vol. 133, Pt. II, p. 36, and Pt. III, p. 48 (1931).

† 'Ber. deuts. chem. Ges.,' vol. 34, p. 3249 (1900).

‡ Auwers, Hinterseber, and Treppmann, 'Liebigs Ann.,' vol. 410, p. 257 (1915).

(*b*) The sample of 1 : 3-*cyclohexadiene* was kindly supplied by Dr. E. H. Farmer, of the Royal College of Science. It boiled at 80·4° and was redistilled immediately before use. Its density immediately after distillation was $d_4^{20} = 0 \cdot 8400$, but after standing for some hours this value increased to 0·8445. For a sample shown to be free from the 1 : 4 compound and from *cyclo*hexene, Harries* gives $d_{20}^{20} = 0 \cdot 8421$, which reduces to $d_4^{20} = 0 \cdot 8406$, whilst Willstätter† found for material of similar purity $d_4^{20} = 0 \cdot 8404$.

Refractive Dispersion.—By using the methods already described‡ the refractive indices of *cyclo*hexene have been measured for 23 wave-lengths in the visual range and for 44 in the photographic range. Similarly the refractive indices of *cyclo*hexadiene have been measured for 24 wave-lengths in the visual range and for 24 in the photographic range. The experimental error is of the order of 5 units in the fifth place of decimals for the visual readings, and 2 or 3 units in the fourth place of decimals§ for the photographic readings. The results are set out in Tables I to III, and have been plotted in fig. 1, together with the values for *cyclo*hexane and for benzene.

An inspection of this figure reveals at once a striking contrast between the course of the curves in the visible and ultra-violet regions of the spectrum. In the visible region the curves *b* and *c* for the two unsaturated hydrocarbons, C_6H_{10} and C_6H_8, lie uniformly between the curves *a* and *d* for the saturated and aromatic hydrocarbons, C_6H_{12} and C_6H_6. Thus the difference at a given wave-length between the refractive indices of *cyclo*hexane and *cyclo*hexene bears a constant ratio to the corresponding difference between *cyclo*hexene and benzene. The indices for *cyclo*hexene are lower than would be expected on the assumption that the three double bonds in benzene produce equal increments of *refractive index*, although the indices of 1 : 3-*cyclo*hexadiene at longer wave-lengths are in accordance with such an assumption. Equal increments are observed, however, in the *molecular refractions*, in which a correction is made for the density of the liquid. As the ultra-violet region is approached the curve *b* for *cyclo*hexene rises only a little more rapidly than the curve *a* for *cyclo*hexane; but the curve *c* for *cyclo*hexadiene rises much more rapidly, and actually crosses the curve *d* for benzene at about 3030 A. This remarkable observation will be discussed in a subsequent paper, with special reference to its bearing on the phenomenon of "optical exaltation."*

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* 'Ber. deuts. chem. Ges.,' vol. 45, p. 809 (1912).

† Willstätter and Hatt, 'Ber. deuts. chem. Ges.,' vol. 45, p. 1468 (1912).

‡ Lowry and Allsopp, 'Proc. Roy. Soc.,' A, vol. 126, p. 165 (1929); *ibid.*, vol. 133, p. 26 (1931).

§ *Cf.* Lowry and Henderson, 'Proc. Roy. Soc.,' A, vol. 136, p. 471 (1932).

Comparison with Previous Measurements.—(*a*) *Cyclohexene.* Auwers (*loc. cit.*) gives for the refractive indices of *cyclo*hexene at 15·1° C. the following values :—

$$n_{\alpha} = 1{\cdot}44653, \quad n_{D} = 1{\cdot}44921, \quad n_{\beta} = 1{\cdot}45620, \quad n_{\gamma} = 1{\cdot}46194.$$

Zelinsky and Zelikow (*loc. cit.*) give $n_D^{27} = 1{\cdot}4428$. In order to eliminate the influence of inequalities in the temperature of measurement, the molecular

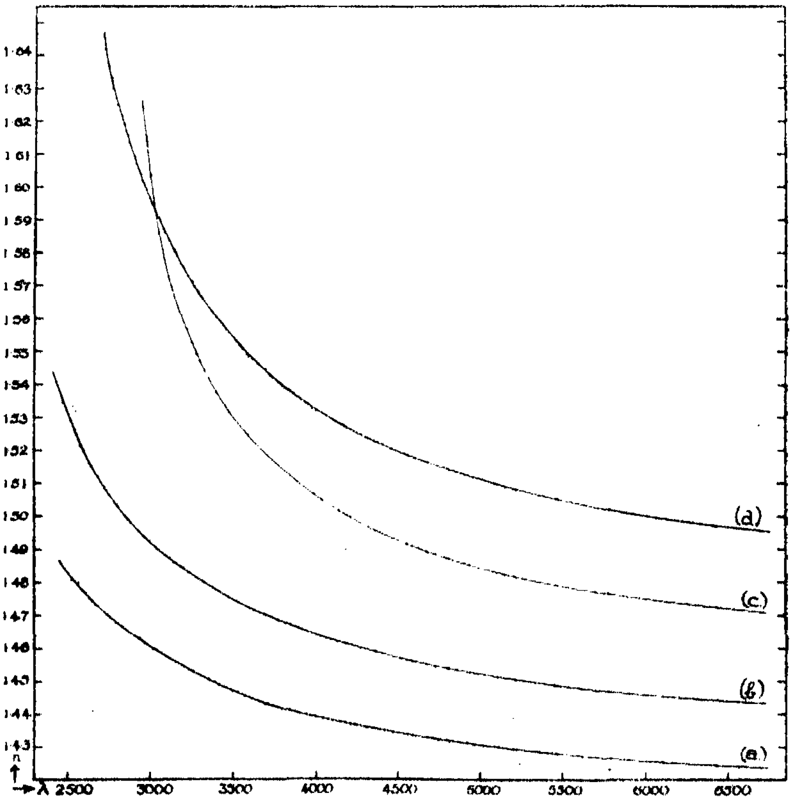

FIG. 1.—Refractive dispersion of (*a*) *cyclo*hexane ; (*b*) *cyclo*hexene ; (*c*) 1 : 3-*cyclo*hexadiene ; (*d*) benzene.

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* [Note added in proof, November, 1933.—Brühl predicted in 1907 ('J. Chem. Soc.,' vol. 91, p. 119) that 1 : 3-*cyclo*hexadiene, unlike the 1 : 4-isomer (in which the double bonds are not conjugated), "would exercise an increased optical effect," and this prediction appears to have been accepted very widely as if it were an established fact. The data now recorded show that, in direct opposition to Brühl's prediction, this hydrocarbon does not give rise to optical exaltation in the visible spectrum, *e.g.*, $M_D = 35{\cdot}20$ (obs.), $35{\cdot}24$ (calc.).]

Table I.—Refractive Indices of Cyclohexene and of 1 : 3-Cyclohexadiene at 20° C.

Pulfrich Refractometer Readings.

Wave-length* λ.	Refractive indices.				Wave-length* λ.	Refractive indices.			
	Cyclohexene.		1 : 3-Cyclohexadiene.			Cyclohexene.		1 : 3-Cyclohexadiene.	
	n. observed.	O—C × 10⁴.	*n.* observed.	O—C × 10⁴.		*n.* observed.	O—C × 10⁴.	*n.* observed.	O—C × 10⁴.
Li 6707·86	1·44335	+0·8	1·47094	+1·3	Cu 5153·26	1·45090	—0·6	1·48230	—1·0
Cd 6438·47	1·44422	+0·2	1·47226	+1·1	Cu 5105·55	1·45125	—0·6	1·48296	—0·3
Zn 6362·34	1·44450	+0·2	1·47261	+0·4	Cd 5085·82	1·45140	—0·7	1·48314	—0·9
Li 6103·6	1·44546	+0·2	1·47403	—0·9	Ba 4934·10	1·45259	—1·1	1·48512	—0·5
Na 5895·93	1·44644	—0·5	1·47548	—0·5	Zn 4810·53	1·45377	+0·5	1·48694	—0·6
Hg 5790·66	1·44698	—0·3	1·47633	+0·1	Cd 4799·91	1·45388	—0·2	1·48718	+0·1
Cu 5782·15	1·44704	—0·1	1·47641	+0·2	Zn 4722·16	1·45467	+0·3	1·48848	+0·9
Cu 5700·24	1·44745	—0·4	1·47706	+0·2	Zn 4680·14	…	—	1·48914	+0·3
Ag 5471·51	1·44879	—0·2	1·47903	—0·3	Cd 4678·15	1·45515	+0·7	1·48917	+0·3
Hg 5460·73	1·44885	—0·2	1·47910	—0·6	Li 4603·0	1·45593	+0·7	1·49058	+1·0
Cu 5220·06	1·45044	—0·3	1·48164	—0·1	Ba 4554·04	1·45653	+1·5	1·49145	+0·5
Ag 5209·04	1·45050	—0·6	1·48175	0·2	Hg 4358·34	1·45873	+0·2	1·49542	—0·9

* The wave-lengths for the visual readings in Tables I to III are taken from the 'International Critical Tables,' vol. 5 (1929). For the photographic readings, the iron lines are either secondary (II) or tertiary (III) standards selected by Fabry ('International Critical Tables,' vol. 5, pp. 275–276 (1929)), or those recorded by Burns ('Z. wiss. Photogr.,' vol. 12, pp. 207–236 (1913)). The tungsten lines throughout are those given by Belke ('Z. wiss. Photogr.,' vol. 17, p. 132 (1917) and vol. 17, p. 144 (1918)).

refractivities, $M_D = 27·01$ and 26·98, deduced from these refractive indices, may be compared with the value, $M_D = 26·99$, calculated from our own readings.

(*b*) *Cyclohexadiene.*—The refractive indices of a specially prepared sample of 1 : 3-*cyclo*hexadiene, at 20°, are given by Harries (*loc. cit.*) as follows :—

$$n_\alpha = 1·47113,\ n_D = 1·47555,\ n_\gamma = 1·49593,\ M_D = 26·82.$$

Willstätter and Hatt (*loc. cit.*) found at 20° :—

$$n_\alpha = 1·47025,\ n_D = 1·47439,\ n_\beta = 1·48516,\ n_\gamma = 1·49491,\ M_D = 26·77.$$

The refractive index $n_D^{20} = 1·47548$ now recorded, and the corresponding value of the molecular refraction, $M_D = 26·84$, are very close to those of Harries; but the divergence between these and Willstätter's values is surprisingly large in view of the close concordance of the densities of the three samples.

Table II.—Refractive Indices of Cyclohexene at 20° C.

Photographic Readings.

Thickness of films 6·35 μ, 6·28 μ, 7·40 μ, and 7·43 μ.

λ.	Refractive index.		Difference (O—C) × 10⁴.	λ.	Refractive index.		Difference (O—C) × 10⁴.
	n. (obs.)	n. (calc.)			n. (obs.)	n. (calc.)	
Fe 4859·749 II	1·4533	1·4534	—1	Fe 3196·937 B	1·4843	1·4841	+2
W 4578·346	1·4562	1·4561	+1	Fe 3147·792 B	1·4863	1·4860	+3
Fe 4515·337 B	1·4569	1·4568	+1	W 3117·580	1·4874	1·4872	+2
Fe 4367·583 III	1·4586	1·4586	±	Fe 3098·191 B	1·4876	1·4800	—4
W 4269·399	1·4598	1·4599	—1	W 3073·287	1·4889	1·4890	—1
Fe 4176·567 B	1·4613	1·4612	+1	W 3034·204	1·4904	1·4907	—3
Fe 4127·611 III	1·4617	1·4619	—2	Fe 2996·391 B	1·4920	1·4924	—4
Fe 4087·102 B	1·4625	1·4626	—1	Fe 2959·906 B	1·4937	1·4942	—5
Fe 4001·667 B	1·4637	1·4638	—1	Fe 2923·852 B	1·4952	1·4961	—9
Fe 3920·849 B	1·4654	1·4654	±	W 2876·936	1·4978	1·4986	—8
W 3881·402	1·4662	1·4661	+1	Fe 2843·629 B	1·4997	1·5005	—8
Fe 3843·261 II	1·4669	1·4668	+1	W 2793·100	1·5031	1·5036	—5
W 3768·448	1·4683	1·4683	±	Fe 2750·145 B	1·5062	1·5064	—2
Fe 3697·436 B	1·4700	1·4698	+2	Fe 2720·202 B	1·5082	1·5085	—3
Fe 3628·094 B	1·4713	1·4714	—1	Fe 2675·287 B	1·5121	1·5119	+2
W 3597·271	1·4722	1·4721	+1	Fe 2636·489 B	1·5153	1·5150	+3
Fe 3533·196 B	1·4737	1·4737	±	W 2560·138	1·5233	1·5234	—1
Fe 3471·914 B	1·4754	1·4754	±	Fe 2535·610 B	1·5259	1·5252	+7
Fe 3413·136 III	1·4773	1·4770	+3	W 2499·697	1·5306	1·5298	+8
Fe 3323·741 B	1·4800	1·4798	+2	W 2466·858	1·5345	1·5347	—2
W 3270·269	1·4815	1·4815	±	W 2455·516	1·5366	1·5365	+1
Fe 3225·790 II	1·4832	1·4831	+1	W 2424·228	1·5408	1·5412	—4

Table III.—Refractive Indices of 1 : 3-Cyclohexadiene at 20° C.

Photographic Readings.

Thickness of films 3·17 μ and 3·09 μ.

λ.	Refractive index.		Difference (O—C) × 10⁴.	λ.	Refractive index.		Difference (O—C) × 10⁴.
	n. (obs.)	n. (calc.)			n. (obs.)	n. (calc.)	
W 4394·092	1·4949	1·4947	+ 2	Fe 3471·27 B	1·5317	1·5331	— 14
W 4316·821	1·4966	1·4964	+ 2	Fe 3389·748 B	1·5376	1·5402	— 26
W 4207·056	1·4994	1·4993	+ 1	Fe 3292·590 B	1·5469	1·5507	— 38
W 4142·261	1·5014	1·5011	+ 3	Fe 3276·477 B	1·5490	1·5528	— 38
W 4037·725	1·5045	1·5043	+ 2	Fe 3191·666 B	1·5592	1·5652	— 60
Fe 3983·960 III	1·5068	1·5061	+ 7	Fe 3125·661 II	1·5697	1·5778	— 81
Fe 3884·362 III	1·5103	1·5099	+ 4	Fe 3116·632 B	1·5716	1·5798	— 82
Fe 3838·259 B	1·5121	1·5118	+ 3	W 3049·694	1·5859	1·5972	—113
Fe 3743·471 B	1·5161	1·5161	±	W 2997·794	1·6026	1·6154	—128
Fe 3675·569 III	1·5183	1·5180	+ 3	W 2992·932	1·6036	1·6173	—137
Fe 3582·202 III	1·5245	1·5251	— 6	Fe 2947·661 B	1·6236	1·6391	—155
Fe 3497·112 III	1·5297	1·5311	—14	Fe 2944·400 B	1·6244	1·6410	—166

The only previous measurements of refractive indices in the ultra-violet for either compound are those of Voellmy* for *cyclo*hexene at 16·2°. He records values, apparently interpolated, for the refractive indices at 12 integral wave-lengths between 4340 A. and 2250 A. The molecular refraction of Voellmy's sample is given as $M_D = 27 \cdot 04$; but in the ultra-violet his values at 16° differ irregularly, and by as much as 0·0097, from our (calculated) values for 20°. The concordance of the molecular refractions of Auwers and of Zelinsky with our own values indicates that the refractive indices now recorded are more trustworthy than those of Voellmy, whose observations on *cyclo*hexane and on benzene exhibit discrepancies of the same magnitude as in *cyclo*hexene.†

Absorption Spectra.—Since the two unsaturated hydrocarbons now under consideration (unlike *cyclo*hexane) exhibit a well-marked selective absorption in the readily accessible ultra-violet region, the molecular extinction coefficients of solutions of *cyclo*hexene and *cyclo*hexadiene in *cyclo*hexane were determined (i) in the range of wave-lengths covered by the iron arc, or by a tungsten-steel spark, either with a polarization photometer or with a small "Spekker" photometer, (ii) at shorter wave-lengths by the method of "variable exposure" employed by Henri. The latter method depends on the relationship,

$$\text{optical density, } d = n \log_{10} (t/t_0),$$

where t and t_0 are the times necessary to produce equal blackening on a photographic plate illuminated alternately through equal thicknesses of solution and solvent, whilst n is a constant depending on the type of plate. In the present experiments, Imperial "Special Rapid" plates were sensitized by a thin film of light machine-oil, and n was determined by making the observed points lie on the curve obtained by the photometric methods. Very good agreement was obtained by using the value $n = 0 \cdot 7$. This constant was therefore used in experiments in which the range of observations was extended to the limit of the aluminium spark spectrum at 1850 A. At intermediate wave-lengths a copper spark was employed. The molecular extinction-coefficients (together with Henri's‡ values for benzene) are plotted against wave-lengths in fig. 2.

(*a*) *Cyclohexene.*—The curve for *cyclo*hexene indicates the existence of (i) a strong band, with a maximum lying just beyond the limits of observation,

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* 'Z. phys. Chem.,' vol. 127, p. 305 (1927).

† Parts II and III, *loc. cit.*

‡ "Etudes de Photochimie," p. 116 (1919).

$\log \varepsilon = 3\cdot60$ at 1850 A., (ii) a broad "step-out," from 2200 A. to 3000 A., at an intensity about ten thousand times less. This step-out could perhaps be attributed to weaker bands, *e.g.*, at 2800 A. to 2400 A. with maxima ranging from $\log \varepsilon = -0\cdot8$ to $-0\cdot2$, superposed on the foot of the band of shorter wave-length.

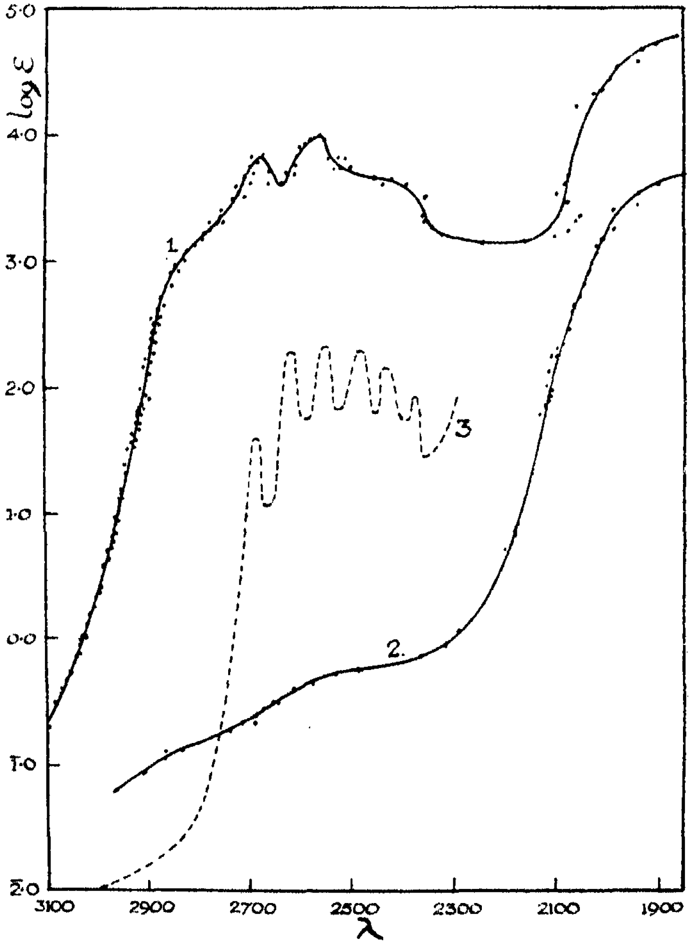

FIG. 2.—Molecular extinction coefficients of (1) 1 : 3-*cyclo*hexadiene; (2) *cyclo*hexene; (3) benzene (Henri's data) in *cyclo*hexane solutions.

In this connection it is of interest to notice that the absorption curve for trimethylethylene, $CMe_2 : CHMe$, in *cyclo*hexane (which will be recorded elsewhere)* shows a step-out over the same range of wave-lengths, but of intensity about 10 times weaker. The step-out in trimethylethylene is followed by a steep rise to the level of the maximum (log $\varepsilon = 3 \cdot 7$ at 1970 A.) in *cyclo*hexene; but the maximum was not quite reached within the limits of our measurements. These singularities have been confirmed by similar observations made by Lüthy* for solutions of the same hydrocarbon in hexane. We therefore conclude that the maximum now recorded in *cyclo*hexene at 1850 A. and the step-out at 2800 A. to 2400 A. are both due to the unsaturated olefinic system, since they correspond so closely to analogous singularities in the curve for trimethylethylene.

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* 'Trans. Faraday Soc.,' Jan., 1934.

(*c*) *Cyclohexadiene.*—The absorption spectrum of 1 : 3-*cyclo*hexadiene also contains a very strong band with a maximum lying just beyond the limits of observation; but the observed maximum of absorption, log $\varepsilon = 4 \cdot 7$ at 1850 A., is at least ten times more intense than that recorded for *cyclo*hexene. Moreover, the step-out at longer wave-lengths has been replaced by a strong band with two well-defined maxima, log $\varepsilon = 3 \cdot 98$ at 2560 A. and log $\varepsilon = 3 \cdot 82$ at 2675 A. The band at $\lambda < 1850$ may again be attributed to the simple ethylenic bond, intensified by the presence in the molecule of a second similar system; but the ultra-violet band at 2650 A. must be attributed definitely to the conjugated system, since it does not occur in compounds containing unconjugated double bonds. This conclusion is confirmed by the fact that bands of similar wave-length are produced by the triply-conjugated double bonds of benzene, fig. 2. The structure of the band, with its characteristic twin maxima, also suggests that it is produced by a completely new electronic configuration in the molecule, and not to a mere displacement towards lower frequencies of the original band due to the olefinic electrons, as has been assumed to take place by Henri† and others.

Dispersion Equations.—(*a*) The data for cyclohexene set out in Tables I and II can be represented from $\lambda = 6708$ A. to $\lambda = 3034$ A. by means of the equation :—

$$n^2 = 0 \cdot 97487 + \frac{1 \cdot 07441\,\lambda^2}{\lambda^2 - 0 \cdot 012226} + \frac{0 \cdot 00327\,\lambda^2}{\lambda^2 - 0 \cdot 056406}. \qquad \text{(I)}$$

At wave-lengths less than 3034 A., however, a "damping factor" (which does not affect even the fifth place of decimals at wave-lengths greater than 3000 A.) must be added to the denominator of the low-frequency term in order to keep the curve of differences of observed and calculated values even approximately along the zero axis. The complete equation then becomes :—

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* 'Z. phys. Chem.,' vol. 107, p. 285 (1923).

† *Loc. cit.*, chap. V.

$$n^2 = 0\cdot97487 + \frac{1\cdot07441\,\lambda^2}{\lambda^2 - 0\cdot012226} + \frac{0\cdot00327\,\lambda^2\,(\lambda^2 - 0\cdot056406)}{(\lambda^2 - 0\cdot056406)^2 + 0\cdot0000804\,\lambda^2}. \qquad \text{(II)}$$

(*b*) In a similar way, the refractive indices of 1 : 3-*cyclo*hexadiene, as set out in Tables I and III, can be represented from λ = 6708 A. to λ = 3700 A. by means of the equation :—

$$n^2 = 1\cdot06977 + \frac{0\cdot973295\,\lambda^2}{\lambda^2 - 0\cdot012226} + \frac{0\cdot0779625\,\lambda^2}{\lambda^2 - 0\cdot072900}, \qquad \text{(III)}$$

but at wave-lengths below 3700 A. the values thus calculated become increasingly too large and no simple modification now suffices to produce a satisfactory agreement in this region.

(*c*) In the region of complete transparency, the agreement between the observed values and those calculated from equations (I) or (II) for *cyclo*hexene or from (III) for *cyclo*hexadiene is remarkably good. Thus (i) for (I) and (II), for 49 wave-lengths between 6708 and 3225 A., the mean difference is only

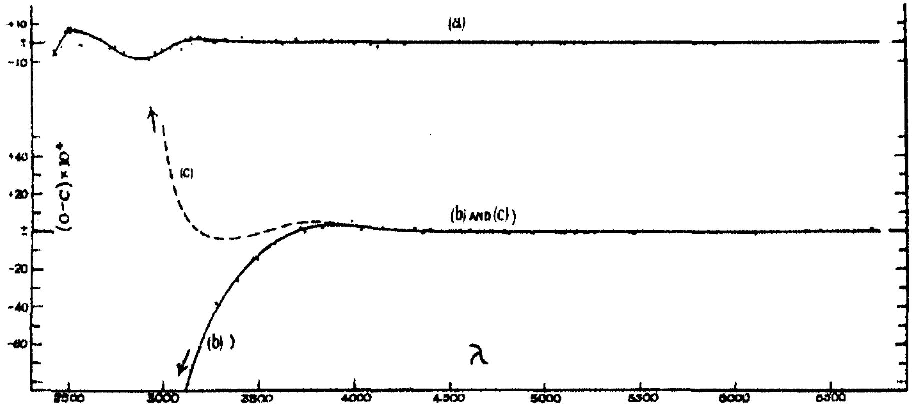

Fig. 3.—Difference curves (*a*) *cyclo*hexene ; (*b*) and (*c*) 1 : 3-*cyclo*hexadiene.

± 0·00008 and the " mean error " only + 0·00003 ; for the 23 visual readings which can be given to five places of decimals, the corresponding values are ± 0·00005 and − 0·000002. As the region of absorption is approached and penetrated, however, the agreement becomes less satisfactory, and two " loops " appear in the difference curve, fig. 3, *a*, which cannot in this case be removed by the addition of a damping-factor in the denominator of the low-frequency term such as was employed in similar circumstances for benzene* and nicotine.* (ii) For equation (III) the mean difference and "mean error" for 34 wave-lengths between 6708 and 3700 A. are ± 0·00011 and + 0·000073 respectively, whilst for the 24 visual readings they reduce to ± 0·00006 and − 0·000002. Below 3700 A., however, the agreement ceases, and the difference curve, fig. 3, *b*, diverges rapidly from the axis. The addition of a "damping factor" to the denominator of the low frequency term of equation (III), whilst restoring this difference curve to a position lying about the zero axis, still leaves serious divergences from it, as is shown by the broken curve in fig. 3, *c*, which is plotted from the equation :—

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* Part III.

$$n^2 = 1{\cdot}06545 + \frac{0{\cdot}975677\lambda^2}{\lambda^2 - 0{\cdot}012226} + \frac{0{\cdot}079933\lambda^2(\lambda^2 - 0{\cdot}072900)}{(\lambda^2 - 0{\cdot}072900)^2 + 0{\cdot}000778\lambda^2}.$$

(*d*) Equations (II) and (III) are both unsatisfactory in the region of absorption, where the theory of damped vibrations breaks down as completely as it does for rotatory dispersion† ; but they represent the refractive dispersions of the two compounds with remarkable accuracy in the region of complete transparency. Each equation includes :—

(i) *A constant term*, A, corresponding theoretically to the square of the refractive index at infinitely long wave-lengths.

(ii) *A partial refraction of high frequency*, B, with a natural period in the Schumann region at 1106 A.

(iii) *A partial refraction of low frequency*, C, with a characteristic frequency at 2375 A. for *cyclo*hexene and at 2700 A. for 1 : 3-*cyclo*hexadiene.

In each equation, the high frequency term B and the constant term A are of similar magnitude. The fact that the constant term is 10% higher in *cyclo*hexadiene than in *cyclo*hexene is compensated by the fact that the term B is 10% lower than in *cyclo*hexene, so that the total refraction due to these two terms, A + B, is approximately the same for each compound. The main difference between their refractive indices is therefore to be found in the ultraviolet term C. Thus, at wave-lengths in the visible spectrum, term C in *cyclo*hexene is 300 times less than term B ; in benzene‡ and in nicotine the ratio of the corresponding terms is 1 : 100 ; but in *cyclo*hexadiene the ratio has increased to 1 : 9. The much-enhanced contribution of the low-frequency term C explains the increase in refractive index which occurs when the second double-bond is introduced into the ring system of *cyclo*hexene; the longer wave-length of its characteristic frequency accounts for the much steeper rise in the refractive indices as shorter wave-lengths are approached.

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* Lowry and Allsopp, 'J. Chem. Soc.,' p. 1613 (1932).

† *Cf.* Lowry and Hudson, 'Phil. Trans.,' A, vol. 232, p. 117 (1933).

‡ In equation (VI) for benzene, as recorded on pp. 53 and 59 of Part II, the constant 0·06143 should read 0·006143.

Relation between Dispersion and Absorption.—It is now possible to correlate the refractive dispersion with the absorption spectra of the two compounds. The refractive dispersion of the saturated six-membered ring in *cyclo*hexane was shown (Part II) to be controlled by a single characteristic frequency at about 1100 A., where a very intense absorption band may be postulated, although it cannot yet be demonstrated experimentally. In *cyclo*hexene, despite the presence of the strong absorption band at 1850 A., the refractive dispersion is still controlled almost entirely by a frequency which is very close to that in the equation for *cyclo*hexane, namely, at 1092 A., that is, presumably, by the same absorption band. It is only at shorter wave-lengths that the second, low-frequency term B is effective. The wave-length 2375 A. of the corresponding characteristic frequency falls within the region covered by the ultra-violet absorption bands now recorded for this compound, which have been attributed to the olefinic radical, although the displacement of 500 A. to the long wave-length side of the principal maximum of absorption suggests that it is a mean value corresponding to contributions from two absorption centres, one at 1850 A. and the other in the " step-out " which has been recorded in fig. 2. In any case, the influence of the single ethylenic bond on the refraction is obviously small, except in the immediate neighbourhood of the absorption band to which it gives rise, and, indeed, it was only detected when the measurements were carried into the region covered by this band.

For *cyclo*hexadiene the position is quite different. Even in the visible spectrum, two variable terms, B and C, are required in the equation of refractive dispersion in order to obtain agreement between observed and calculated values. The characteristic frequency of the Schumann term B can again be identified with that observed in *cyclo*hexane. The characteristic frequency of the low frequency term, C, which falls at 2700 A., obviously represents (as for benzene) a mean value for the various components of a complex absorption system. It is interesting, however, that no partial refraction seems to be required to correspond with the intense band at 1850 A., although in the equation for benzene, recorded in Part III, the Schumann term is replaced entirely by one whose characteristic frequency lies at a wave-length in this region of the spectrum.

It can, therefore, be concluded that, whilst the feeble absorption of *cyclo*hexene, as represented by the "step-out" on the absorption curve, only influences the refraction inside the region of absorption, the strong absorption of *cyclo*hexadiene in the same region produces a partial refraction even in the visible spectrum, and is responsible both for the higher refractive indices of the conjugated compound, and for their very rapid increase as the ultra-violet region of the spectrum is penetrated.

The author desires to place on record his indebtedness to the Department of Scientific and Industrial Research for providing a Research Assistantship during the period in which the investigation described in the present paper was carried out.

Summary.

(1) Values are given for the refractive indices, at 20°, of *cyclo*hexene at 67 wave-lengths between 6708 A. and 2420 A., and of 1 : 3-*cyclo*hexadiene at 48 wave-lengths between 6708 A. and 2940 A.

(2) Molecular extinction coefficients for both compounds in solution in *cyclo*hexane are also recorded. The absorption curve for *cyclo*hexene contains a maximum, $\log \varepsilon = 3 \cdot 7$ at 1850 A., with a "step-out," 10,000 times less intense, between 2300 A. and 2800 A., both of which are attributed to the ethylenic bond. The curve for 1 : 3-*cyclo*hexadiene contains a similar maximum, $\log \varepsilon = 4 \cdot 75$ at $\lambda = 1850$ A., but with two new maxima at $\log \varepsilon = 4 \cdot 0$ at 2560 A., and $3 \cdot 8$ at 2680 A. respectively, which are a new band system characteristic of the conjugated double bonds.

(3) The refractive indices of *cyclo*hexene between 6708 A. and 3034 A. can be represented by the equation :—

$$n^2 = 0 \cdot 97487 + \frac{1 \cdot 07441 \lambda^2}{\lambda^2 - 0 \cdot 012226} + \frac{0 \cdot 00327 \lambda^2}{\lambda^2 - 0 \cdot 056406};$$

but below the latter wave-length, a damping factor in the denominator of the low-frequency term is necessary in order to obtain even approximate agreement between observed and calculated values. Similarly the refractive indices of 1 : 3-*cyclo*hexadiene can be represented between 6708 A. and 3700 A., by the equation :—

$$n^2 = 1 \cdot 06977 + \frac{0 \cdot 973295 \lambda^2}{\lambda^2 - 0 \cdot 012226} + \frac{0 \cdot 0779625 \lambda^2}{\lambda^2 - 0 \cdot 072900}.$$

Each equation contains a high-frequency term corresponding to the partial refraction of a hypothetical band in the Schumann region, at the same wave-

length as that deduced for *cyclo*hexane, and a low-frequency term which is the partial refraction of the absorption bands observed in the ultra-violet.

(4) The partial refraction of the ultra-violet absorption band of 1 : 3-*cyclo*hexadiene is much larger than the corresponding partial refraction for *cyclo*hexene. It is responsible for the increase of refractive index which accompanies the introduction of the second double bond into the 6-ring, and also accounts for a rapid increase observed in the refractive indices of *cyclo*hexadiene at short wave-lengths.

The Aggregation of Colloidal Electrolytes from Transport Number and Conductivity Measurements: Some Benzidine Dyes.

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(Communicated by F. G. Donnan, F.R.S.—Received October 13, 1933.)

I. *Introduction.*

In previous communications* from this laboratory some of the properties of benzopurpurine 4B and the isomer prepared from *m*-tolidine have been described. These two dyes (which will be referred to briefly as the "4B" and "meta" dye, respectively) differ in chemical constitution only by the position of two methyl groups, but show striking differences in their colloidal properties.* Further, the 4B dye is a well-known cotton substantive dye, while the meta dye is not sufficiently substantive to be of any practical value. A comprehensive study of the solutions of these two substances is therefore of considerable interest, for it should not only extend our knowledge of colloidal electrolytes, but should throw some light on the theory of dyeing.

In the previous communications it was shown that the viscosities, conductivities, and osmotic pressures of the half per cent. (N/70) solutions of the two dyes are about the same. On the other hand, the 4B dye was found to be stopped by much coarser ultrafilters, and is flocculated completely by small concentrations of electrolytes, while the meta dye is never completely flocculated, even by very large concentrations.

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* Robinson and Mills, 'Proc. Roy. Soc.,' A, vol. 131, pp. 576, 596 (1931).

To explain these results it was assumed that both dyes existed as sodium ions and anionic micelles, the micelles in the meta dye consisting of about ten anions (a value obtained from osmotic pressure measurements in the presence of NaCl), while the 4B dye was assumed to contain considerably larger micelles. This explanation, however, meets with the following serious difficulty: On this assumption we should expect, from Stokes' law, that the 4B micelles would be more mobile (*cf.* Section III, B, below), and the 4B dye would then have a higher conductivity than the meta dye. In order to make the conductivities of the two dyes more nearly equal, it would be necessary to assume that the 4B dye micelles contained more included sodium than the meta micelles, but this would make the osmotic pressure of the 4B dye considerably less than that of the meta. Conductivities and osmotic pressures, therefore, indicate that the 4B and meta dyes are in about the same state of aggregation in their N/70 solutions. It will accordingly be seen that there is a need for further evidence on the size and constitution of these micelles.

Several of the well-known methods of determining the size of colloidal particles are not applicable to these amicronic colloidal electrolytes. Thus their diffusion coefficients in pure solutions cannot give the particle size, owing to the complications introduced by the electrical forces between the oppositely charged particles, which have been discussed by Hartley and Robinson.* It was possible to obtain a value for the particle size of the meta dye by measuring the diffusion coefficient in the presence of excess electrolyte, but the 4B dye was too sensitive to electrolytes to make this method applicable.

It is therefore necessary to measure some other quantity, which is sensitive to changes in aggregation. Transport numbers fulfil this condition. If we have a colloidal electrolyte consisting of two radicals, and if the negative radical, for example, aggregates to form negative micelles, with or without the inclusion of some of the positive radicals, then the transport number of the negative radical will increase with increasing aggregation, as is shown in Section III, B. In what follows we shall describe transport number measurements on these dyes, using the moving boundary method, together with more accurate conductivity measurements than those of Robinson and Mills, and we shall discuss the constitution of the micelles in the light of this new evidence, which makes it necessary to modify the earlier conclusions.

The dyestuff Bordeaux Extra was included in order to compare the behaviour of the meta and 4B dyes with that of a dye which was thought to be more nearly in true solution,* and which would consequently be expected to show considerably different properties.

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* 'Proc. Roy. Soc.,' A, vol. 134, p. 20 (1931).

II. EXPERIMENTAL.

A.—*The Dye Solutions.*

The samples of the 4B and meta dyes, specially prepared by the Dyestuffs Group, Imperial Chemical Industries, from pure intermediates, were purified by the method of Robinson and Mills.† The Bordeaux Extra was of commercial quality, supplied by the courtesy of the I.G. Farbenindustrie, and it was first purified by the same treatment. The conductivity of the ultrafiltrate, however, showed that some highly conducting coloured impurity was still present. This was removed by dissolving the dye three times in hot conductivity water and reprecipitating by cooling (crystals are not obtained). The purity of the dye samples is discussed in Section III, C, below.

The more concentrated dye solutions were made up by dissolving some of the solid dye in approximate volumes of boiling conductivity water, in order to exclude atmospheric CO_2. All solutions were stored in conical Pyrex flasks, having ground-glass stoppers fitted with syphons and soda lime tubes to exclude CO_2. Dilute solutions were prepared from the concentrated ones, using standardized pipettes and volumetric flasks. Although the conductivity of the half per cent. solutions of these dyes does not alter appreciably on exposure to the air for several hours, exposures to the air when filling cells, etc., were limited to a few seconds.

All vessels used in the purification and storing of solutions were of Pyrex, previously cleaned with chromic acid, followed by soaking for at least several days in several changes of conductivity water.

The concentrations of the more concentrated solutions were determined by evaporating to dryness. Neale and Hanson‡ have criticized the method of drying used by Robinson and Mills and claim that after drying to constant weight in an air oven at 105°, as the latter did, further moisture is removed by drying *in vacuo* over P_2O_5 at 110°. In order to remove all such possible sources of error, the following procedure was adopted: 25 cc. of dye solution were evaporated in a wide-mouthed weighing bottle (5 cm. in diameter) on a water bath. This was then dried in a vacuum desiccator at room temperature, over P_2O_5. Constant weight was usually reached in 2 weeks, but the samples were all desiccated for at least 3 or 4 weeks.

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* Robinson and Mills, *ibid.*, vol. 131, p. 609 (1931).

† 'Proc. Roy. Soc.,' A, vol. 131, p. 579 (1931).

‡ 'Nature,' vol. 129, p. 761 (1932).

No further change in weight was found after desiccating these samples further at 110° and 130° in a special vacuum drying apparatus, in which the dye is heated while the P_2O_5 is kept cold, even after such treatment for six periods of 12 to 40 hours. Subsequent experiments showed that the same weight was obtained by the air oven method of drying, and we can only conclude that the criticism of Neale and Hanson does not apply when using the very thin layers of evaporated dye which were used by Robinson and Mills, and in these experiments. A calcium chloride desiccator should not be used after drying, however, since the dyes were found to take up moisture from the calcium chloride.

Analyses were done in duplicate, with an agreement of 0·2% to 0·1%, the samples weighing from 0·1000 to 0·1500 gram.

B.—*Transport Number Measurements.*

1. *The Moving Boundary Method.*—A general review of the method has been given by MacInnes and Longsworth.[*] The theory has been treated from a somewhat different angle by Hartley and Moilliet,[†] and the following will be based to a large extent on the latter authors' treatment, the same definitions and symbols being used. It has been shown that if a solution such as Na_2R in fig. 1 lies below one of NaX, a sharp boundary *ab* will move downward when a current flows in the direction shown by the signs, provided that the following conditions are satisfied: (*a*) the Na_2R solution must be heavier than the NaX solution; (*b*) the radical R must be faster than the radical X, both in their respective solutions and in any mixture of the two that may arise at the boundary; and (*c*) the disturbing effects of convection, electrolysis products, and endosmosis must be absent.

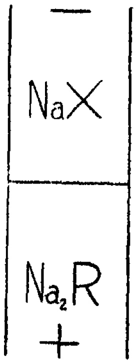

FIG. 1.

R is called the leading radical, Na_2R the leading solute, and NaX and X are called the indicator and indicator radical, respectively. If c_R be the concentration of the leading solute in gram-equivalents per cubic centimetre, and if the boundary advances through V cubic centimetres in *t* seconds, while a current I is flowing, then the transport number T_R of the *leading* radical R is given by

$$T_R = \frac{V \, . \, c_R \, . \, F}{I \, . \, t}, \qquad (1)$$

where F is the faraday.

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[*] 'Chem. Rev.,' vol. 11, p. 171 (1932).

[†] 'Proc. Roy. Soc.,' A, vol. 140, p. 141 (1933).

As has previously been shown,* the concentration of the leading solute Na_2R remains constant on the passage of the current, while the new indicator solution formed below the original position of *ab* must satisfy the well-known relation of Kohlrausch :†

$$\frac{T_R}{c_R} = \frac{T_X^K}{c_X^K}, \tag{2}$$

where the index K refers to the new indicator solution.

Care must be taken to make the initial indicator concentration equal to or less than c_X^K, for if the indicator concentration is initially greater than c_X^K, a dilute solution is formed below a more concentrated one, and concentration convection occurs. This convection not only undoes the automatic adjustment of the indicator, but sweeps up part of the leading solution, thus giving values for T_R that are too high.

2. *Corrections in the Moving Boundary Method.*—The transport numbers obtained with the moving boundary method must be corrected for (*a*) volume changes at the electrodes used, (*b*) volume changes caused by the replacement of one solution by another, and (*c*) the conductivity of the water used in making up the solutions. The solutions studied in this work were so dilute that only (*c*) is of any importance here.

Longsworth‡ has shown that the measured transport number T'_R must be corrected for water conductivity by the formula

$$T_R = T'_R\left(1 + \frac{\kappa_{H_2O}}{\kappa_S}\right), \tag{3}$$

where T_R is the corrected transport number, κ_{H_2O} is the specific conductivity of the water used, and κ_S is the specific conductivity of the Na_2R solution. This correction should be applied to results from both the moving boundary and Hittorf methods, as Longsworth points out.

Longsworth goes on to state that his correction by (3) will never be sufficient, since the leading solution will be progressively contaminated by impurities forced across the boundary by the greater potential gradient obtaining in the indicator. This will be true, however, only if one or more of the anions of the water impurities have higher mobilities than the R radical, when the boundary will progressively slow down. If all the impurity anions are slower than R, the impurities will become concentrated into the region immediately above the boundary, but the "sharpening effect"* will prevent their entering the region below the boundary. The boundary velocity will therefore remain constant, and the water correction will be sufficient.

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* Hartley and Moilliet (*loc. cit.*).

† 'Ann. Physik,' vol. 62, p. 209 (1897).

‡ 'J. Amer. Chem. Soc.,' vol. 54, p. 2741 (1932).

We suggest, therefore, that the Longsworth water correction to transport numbers is as exact as the corresponding correction to the conductivity of the solution in question, provided that the velocity of the boundary remains constant throughout a determination.

3. *The Moving Boundary Cell.*—Fig. 2 is a cross-section of the moving boundary apparatus used in this research, which is that of MacInnes and Brighton,† with certain necessary changes in the electrode vessels. The graduated and calibrated U-tube U contains the dye solution Na_2R, the open cathode chamber C contains the indicator NaX, and the closed chamber A contains an NaCl solution and a reversible anode. The cathode is a loop of platinum wire, surrounded by floating crystals of benzoic acid to neutralize the OH formed electrolytically, and dips into the open tube T. T and the vessel V lengthen the path from the gassing cathode to the U-tube, so that disturbances arising at the cathode do not reach the U-tube. The vessel V is supported by three shortglass legs, not shown in the diagram, and a notch is cut in the bottom of T.

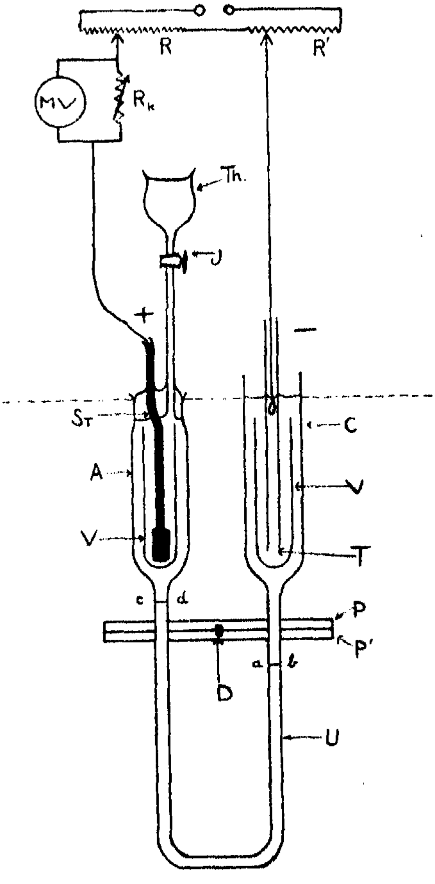

FIG. 2.

The anode chamber A contains an NaCl solution of the same normality as the dye in U, and is closed with a generously lubricated ground-glass stopper St. The thistle funnel Th is also filled with the NaCl solution, and since the stop-cock J is closed during a measurement, mass displacements of liquid in

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[*] *Cf.* Hartley and Moilliet, *loc. cit.*, p. 153.

[†] 'J. Amer. Chem. Soc.,' vol. 47, p. 994 (1925).

the apparatus are impossible. The reversible anode is a cylinder of platinum gauze, plated electrolytically with silver. The vessel V is identical with the one in the cathode chamber, and protects the U-tube from any concentration disturbances arising at the anode.

P and P′ are two glass plates, etched and ground after the pattern of MacInnes and Brighton. One of these is shown in fig. 3. Shaded areas are etched away with HF solution; white areas are carefully ground flat and are generously lubricated. The plates turn on the brass pivot D. The two limbs of the U-tube are cemented into the holes H and H′ of the bottom plate; the electrode chambers A and C are cemented into H and H′ of the upper plate. Picein is used as cement, with a coating of paraffin on the side next to the thermostat water in order to prevent electrical leaks, which are troublesome. The clamp for holding the bottom plate and the method of turning the upper plate have been described by MacInnes and Brighton (*loc. cit.*). The entire apparatus goes in a water thermostat, the level of the water being indicated by the dotted line in fig. 2.

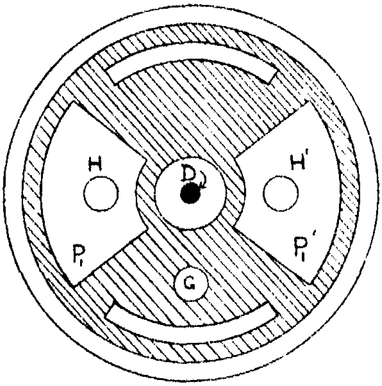

Fig. 3.

The hole G is made in the upper plate only. The procedure followed in forming a boundary is as follows: The upper plate is turned so that G is over H or H′ of the bottom plate. The U-tube is then filled with dye, until it overflows slightly, through G. A long glass tube, with a joint ground to fit G and heavily lubricated, is then inserted, and the whole apparatus is placed in the thermostat. After allowing 5 minutes for thermal expansion to become complete, the upper plate is turned until the excess dye above the U-tube is sheared off by the plateaux, Pl and Pl′, of the upper plate. In so doing, Pl and Pl′ of the bottom plate close the electrode chambers. The electrode chambers are then filled, and the vessels V, the tube T, and the ground-glass stopper St are inserted, care being taken that no air is trapped in the anode vessel. The stop-cock J is left open while the whole apparatus is given half an hour to come to thermal equilibrium. The stop-cock is then closed and the external potential is applied. By taking out very large values in the standard resistance R_K, small current leaks can be detected. If leaks are absent, the upper plate is turned until H and H′ of the two plates coincide, thus forming the boundary.

A Julius suspension for the thermostat, used by MacInnes and Brighton in New York, was not needed.

The current flowing through the cell is kept constant by hand regulation of the two rheostats R and R′, which are of 4000 and 750 ohms resistance, respectively. The current is measured by measuring the drop in potential across a standard resistance R_K (N.P.L. certificate) with a suspended-coil type millivoltmeter, the resistance of which is known. This arrangement for measuring the current is preferable to a milliammeter, because the scale reading on the instrument can be kept at a maximum by varying R_K. The current I was calculated from

$$I = \frac{MV\,(R_K + R_M)}{R_K \,.\, R_M}, \tag{3}$$

where MV is the millivoltmeter reading, R_M is the resistance of the millivoltmeter, and I is given in milliamperes.

The millivoltmeter was found to be sensitive to 0·2% of the maximum scale reading, and the instrument was calibrated against a potentiometer, using several currents. The calibrations with different currents checked within 0·2%.

The U-tube was accurately graduated every half centimetre, and the marks extended all the way around the tube except for gaps in front and at the back. Parallax is avoided by this arrangement, and the boundary is never obscured. The volume of the U-tube traversed by a complete moving boundary determination was determined by weighing the water run out between marks, in quadruplicate, with an average deviation of 0·1%. The volume between each five marks was also determined at the same time. The U-tube was of small cross-sectional area (0·4 square centimetre) in order to dissipate more rapidly the heat developed by the current and thus reduce temperature convection. If the tube is made too small, endosmotic flow along the walls of the tube will blur the boundaries, especially with very dilute solutions, though the closed anode chamber will prevent any mass displacements due to endosmosis. The area chosen proved to be suitable for the entire range of concentrations studied.

In a given measurement the boundary *ab* was timed as it moved down the U-tube, and the volume traversed was plotted against time, on an extended scale, to see that the boundary velocity was remaining constant. The boundary could be timed within 0·1 to 0·2 of a minute, and a complete measurement lasted about 100 minutes, a volume of 3·104 cm. being traversed. The rising boundary *cd* was not timed, since its velocity is governed by the Cl radical in the NaCl solution in the anode chamber. The concentration of this NaCl solution must be so chosen that the new dye solution, built up above the original position of *cd*, is not heavier than the old dye solution in U. An NaCl solution of the same normality as the dye satisfies this requirement.

The results of a typical measurement are given in Table I. The boundary velocity in this and all other measurements was constant. The transport numbers given in the general table of results have all been corrected by the water correction formula of Longsworth (*loc. cit.*), which was considered sufficient in view of the constant boundary velocities.

Table I.—Transport Number T_R of a 0·002708 N Solution of Benzopurpurine 4B—Run I.

Indicator: 0·00120 N sodium benzoate; I is 0·2226 mA.

Time in minutes.	Volume traversed.
0	0
7·1	0·208
14·2	0·416
21·3	0·624
35·6	1·039
50·1	1·455
71·5	2·081
85·5	2·490
106·7 = 6402 seconds	3·104

$$T_R = \frac{3 \cdot 104 \times 96500 \times 0 \cdot 002708 \times 10^{-3}}{0 \cdot 2226 \times 10^{-3} \times 6402} = 0 \cdot 568$$

T_R (corrected for water conductivity) = 0·571

4. *The Indicator Solutions.*—Sodium benzoate solutions were used as indicators for the 4B and meta dyes, and gave sharp boundaries. A slower indicator radical was required for Bordeaux Extra, and α-naphthalene sulphonate was found to be suitable. The boundaries were not so sharp as those between the other two dyes and sodium benzoate, but by means of the dark-line device of Abegg and Gaus* a refractive index boundary could be satisfactorily located.

The sodium benzoate was prepared by neutralizing a hot solution of benzoic acid with CO_2-free NaOH solution, using a few drops of phenolphthalein as indicator. The solution was evaporated nearly to dryness, and the sodium benzoate was crystallized out, filtered off, and dried in an air oven at 110° for several hours. The benzoic acid was B.D.H. "ordinary" quality, recrystallized four times from conductivity water. The sodium α-naphthalene sulphonate was B.D.H. "ordinary" quality, recrystallized four times from conductivity water.

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* ‘Z. phys. Chem.,’ vol. 40, p. 737 (1902).

The effect of indicator concentration on the observed transport number was followed in detail on N/70 solutions of the 4B and meta dyes. Below the Kohlrausch concentration, the observed transport number was independent of the initial indicator concentration, within the precision of the measurements; with indicators that were initially too concentrated, the observed transport numbers were too high.* The procedure adopted in succeeding runs was therefore to choose all indicators from 5% to 30% more dilute than $c_{\mathrm{X}}^{\mathrm{K}}$, and make several determinations, varying the indicator concentration each time. The mean was then taken and corrected for the conductivity of the water. Section II, D, includes the results of the transport number measurements, the precision attained for each normality being indicated by the average deviation from the mean.

C.—*Conductivity Measurements.*

1. *Apparatus.*—The conductivities were measured with an A.C. Wheatstone bridge, consisting of a Tinsley non-inductively wound ratio box of maximum resistance of 10,000 ohms in each arm, a Tinsley non-inductively wound variable four-dial resistance box, reading from 1 to 10,000 ohms (N.P.L. certificate), and a variable condenser in parallel with the latter. The current was supplied from a valve oscillator, which gave two frequencies in the ratio 1 : √2, and a pair of headphones was used for determining the null point. Lead-shielded wire, tested for D.C. leaks, was used for the connections. The lead shieldings and the shieldings of the variable condenser, resistance box, and ratio arms were connected together and earthed.

Conductivities were measured on a 1 : 1 ratio, whenever this could be done without giving a reading of less than 500 ohms. The Wheatstone bridge was calibrated with a second Tinsley non-inductive variable resistance. This revealed a small leads leak of 5,000,000 or 8,000,000 ohms, depending on the frequency, but constant at any one frequency. This leak did not occur with direct current and was evidently due to an imperfection in the insulating material giving rise to a small loss angle. The leak could be corrected for when necessary.

The three types of cells used in covering the range of conductivity from 1×10^{-6} to 2000×10^{-6} reciprocal ohms are shown in fig. 4; (*a*) is for pure water and solutions of specific conductivity less than 150×10^{-6}, has a cell constant of 0·05738, a capacity of 30 cc., and rectangular smooth platinum electrodes each about 3 sq. cm. in area; (*b*) is for solutions of conductivities between 150 and 1000×10^{-6}, has a cell constant of 0·4034, a capacity of 15 cc., and circular grey platinum electrodes, each about 1 sq. cm. in area; (*c*) is for solutions of conductivities above 1000×10^{-6}, has a cell constant of 4·780, a capacity of 35 cc., and circular smooth platinum electrodes, each about 1 sq. cm. in area.

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* *Cf.* Hartley and Moilliet, *loc. cit.*, p. 151.

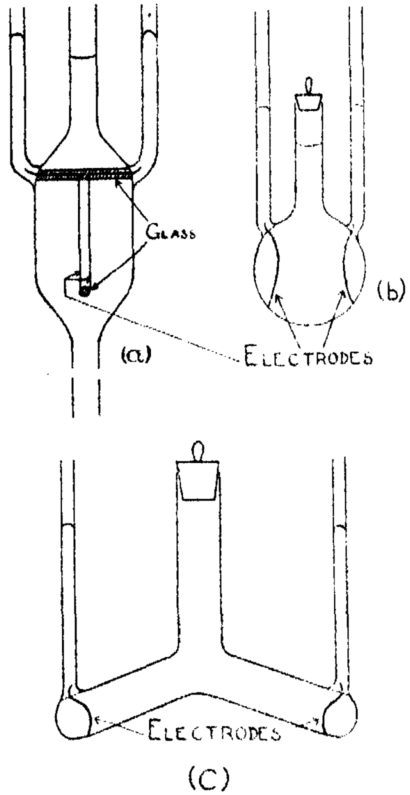

Fig. 4.

The designs of the cells made the Leyden jar capacity leaks negligible when the appropriate cell was used for each solution, as shown by the resistances of the most dilute solutions remaining constant at different frequencies.

Smooth platinum electrodes were used in cell (c), because it was found that with black or grey electrodes reproducible readings could not be obtained on the more concentrated solutions, probably on account of adsorption of the dyes. The use of smooth electrodes undoubtedly introduced polarization effects, though they were reduced by having the electrodes far apart. A polarization correction sufficient for our purposes could, however, be made in the following way. An expression due to Kohlrausch and Holborn[*] may be written in the form, when the frequency is not too great,

$$R = R' - \frac{A}{\omega^2}, \tag{4}$$

where ω is the frequency, R is the true resistance, R′ the apparent resistance, and A is a constant characteristic of the particular solution in the cell. If the apparent resistance R″ is then measured at another frequency, the square of which is twice the square of the first frequency, then (4) yields the following relation

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[*] "Das Leitvermögen d. Elektrolyte," p. 66, Berlin, 1916.

$$R = 2R'' - R'. \tag{5}$$

Polarization corrections were made by means of (5) whenever necessary, but the corrections were never over 0·2%. The presence of polarization was indicated when the resistance of a solution changed with frequency, and the capacity required for a sharp balance also changed.

All null points could be located with a precision of 0·1%. The results of the conductivity measurements are given in Section II, D, the conductivity of each solution being corrected for the conductivity of the water.

2. *Conductivity Water.*—The samples of water used in making up solutions had specific conductivities of from 1×10^{-6} for the dilute solutions to 2×10^{-6} for the more concentrated ones. Since the acid dye H_2R of these dyes is insoluble, it is evident that any acidic contaminations in the conductivity water could lower the conductivity of the solutions quite appreciably by precipitating acid dye. The following test was therefore made on solutions of the meta dye and Bordeaux Extra to see if acidic impurities were introducing any errors into the results. Some water ($\kappa = 1{\cdot}0 \times 10^{-6}$) was made slightly alkaline with NaOH, and its conductivity was measured again (about $1{\cdot}5 \times 10^{-6}$). A dye solution was then prepared with the alkaline water, and its conductivity was measured and corrected for the conductivity of the alkaline water. The conductivity of an equinormal solution made with non-alkaline water was also measured and the appropriate correction applied. The agreement between values with alkaline and non-alkaline water is shown in Table II.

Table II.

	κ (corrected) with alkaline water.	κ (corrected) with non-alkaline water.
Solution I (meta)	$36{\cdot}1 \times 10^{-6}$	$36{\cdot}2 \times 10^{-6}$
Solution II (meta)	$17{\cdot}8 \times 10^{-6}$	$18{\cdot}2 \times 10^{-6}$
Solution III (meta)	$29{\cdot}0 \times 10^{-6}$	$28{\cdot}9 \times 10^{-6}$
Solution IV (Bordeaux Extra)	$8{\cdot}8 \times 10^{-6}$	$8{\cdot}9 \times 10^{-6}$

These results indicate that no appreciable error is introduced by acidic contaminations in the water, for then the values with non-alkaline water would have been considerably lower. Actually, conductivities with non-alkaline water tend to be higher, which is to be expected, since the interionic forces will be slightly increased by the addition of NaOH. The results obtained with alkaline water are not included in the table of results, but they do furnish a good confirmation of the tabulated values.

It is suggested that this procedure should be of general value in conductivity work where electrolytes are very sensitive to traces of acid or basic contamination. A certain error is introduced by adding base or acid beforehand, but it is much smaller than the errors that can arise from a reaction between the water impurity and the electrolyte being studied. Where, as with these dyestuffs, values obtained with adjusted water are not included in the results, but merely used to confirm them, the method seems particularly useful.

3. *The Conductivities of the Ultrafiltrates and the Purity of the Samples.*—Robinson and Mills[*] corrected their conductivity data on the 4B and meta dyes for the conductivities of the ultrafiltrates, which are often assumed to give the conductivities of any impurities present in the intermicellar liquids. This correction was not made in this work, because, as Pauli and Valko[†] have pointed out, the intermicellar liquid of a sol is not identical with its ultrafiltrate, since the ultrafiltrate contains products of membrane hydrolysis. When a solution of Na_2R is filtered through a membrane that stops the R radical but allows the Na to pass, membrane hydrolysis must occur, *i.e.*, H_2R will be left behind and NaOH will be formed in the ultrafiltrate. The ultrafiltrate may therefore have an appreciable conductivity, even if the Na_2R solution is pure. If the filtration were done infinitely slowly, the NaOH concentration would satisfy the Donnan equilibrium condition for the Na_2R solution. For N/70 solutions of these dyes, an approximately 4×10^{-5} N solution of NaOH (the specific conductivity of which would be about 10×10^{-6}) satisfies this condition. Ingraham, Lombard, and Visscher[‡] have shown both theoretically and experimentally that the ultrafiltrates of some plasma proteins are practically in equilibrium with the solution being filtered, even when the filtration was fairly rapid. If, however, the rate of filtration is increased sufficiently, the degree of hydrolysis will be less than that at equilibrium. Such a case is recorded by McBain and McClatchie[§] for Fe_2O_3 sols, though even here the hydrolysis is always appreciable. Some data of Robinson and Mills and a conductimetric titration by the authors on the ultrafiltrate of a 4B dye solution, both indicate that membrane hydrolysis is still appreciable at the rates of filtration used.

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[*] 'Proc. Roy. Soc.,' A, vol. 131, p. 576 (1931).

[†] "Die Elektrochemie der Kolloide," pp. 74–76 (1929).

[‡] 'J. Gen. Physiol.,' vol. 16, p. 637 (1933).

[§] 'J. Amer. Chem. Soc.,' vol. 55, p. 1315 (1933).

Table III is taken from the data of Robinson and Mills,* and gives the ratio $\kappa_t/(\kappa_s - \kappa_t)$ (where κ_s is the conductivity of the Na_2R solution, and κ_t is the conductivity of the ultrafiltrate) at different concentrations of Na_2R. If the conductivities of the ultrafiltrates are caused by impurities in the dye solutions, the ratio should be roughly constant. If, on the other hand, the conductivities are caused at least in part by membrane hydrolysis or contamination from the filter, or both, the ratio should increase considerably with dilution. The results in Table III definitely point to the two latter causes.

Table III.

Approximate normality of dye solution.	Ratio $\kappa_t/(\kappa_s - \kappa_t)$.	
	4B dye.	Meta dye.
	%	%
N/70	2·4	3·3
N/140	2·6	—
N/280	3·6	—
N/500	—	5·8
N/1000	14	—
N/2500	—	13
N/5000	36	—
N/10,000	—	43

The alkalinity of the ultrafiltrate from a N/140 solution of the 4B dye was established by following conductimetrically the effect of adding a very small concentration of HCl. The conductivity of the ultrafiltrate was $2{\cdot}8 \times 10^{-6}$ (all conductivities given here are corrected for that of the water), and that of an approximately 0·00002 N HCl solution was $6{\cdot}5 \times 10^{-6}$. When equal volumes of the two solutions were mixed, the conductivity of the mixture was $2{\cdot}4 \times 10^{-6}$, which definitely shows that the ultrafiltrate was alkaline. Taking the HCl concentration as $1{\cdot}5 \times 10^{-5}$ (from the conductivity), and assuming that all the conductivity of the ultrafiltrate was due to NaOH (the concentration of which would be $1{\cdot}1 \times 10^{-5}$), it was calculated that the conductivity of the resulting mixture of HCl and NaCl should be $1{\cdot}6 \times 10^{-6}$, which, considering the sources of error, agrees fairly well with the experimental value.

Since membrane hydrolysis has been shown to occur when these dyes are ultrafiltered, and since there is also the possibility of the ultrafiltrates being contaminated by exchange adsorption or double decomposition with the membranes, it is clear that ultrafiltration, though useful in detecting large amounts of impurities, cannot be used for quantitative corrections.

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* *Loc. cit.*, pp. 591–592.

The conductivities of the ultrafiltrates of N/70 solutions, corrected for the conductivity of the water, were: meta dye, $6 \cdot 5 \times 10^{-6}$; 4B dye, $3 \cdot 7 \times 10^{-6}$; Bordeaux Extra, 14×10^{-6}. These conductivities are small enough to be accounted for by membrane hydrolysis. It is also shown in Section III, E, that the u_{Na} curves for solutions of the meta dye and Bordeaux Extra confirm the purity of these two dyes, and that the corresponding evidence for the 4B dye, though less conclusive, is also against any considerable contamination.

D.—*Experimental Results.*

All transport number and conductivity measurements were made in a water thermostat at 25°, accurate and constant to 0·03°.

The transport numbers of the R radicals in zero concentrations of the meta dye and Bordeaux Extra were obtained by subtracting 50·1, the equivalent conductivity of sodium at infinite dilution,* from the extrapolated value λ_0, and dividing the remainder by λ_0. The points thus obtained give smooth curves with the experimental T_R values. This procedure does not seem justified with the 4B dye because of the minimum in the experimental part of the T_R curve.

The values of v_R at infinite dilutions of the meta dye and Bordeaux Extra were correspondingly obtained by subtracting 50·1 from λ_0. The u_{Na} ($u_{Na} = \lambda - v_R$) curves were extrapolated to a zero concentration value of

Table IV.—Benzopurpurine 4B.

Normality.	λ.	T_R	Average deviation.	v_R	u_{Na}
			%		
0·01191	74·5	0·653	0·2	48·6	25·9
0·01083	74·8	0·646	0·2	48·2	26·6
0·00794	78·6	0·631	0·2	49·6	29·0
0·00541	82·6	0·608	0·3	50·3	32·3
0·00397	86·1	0·593	0·3	51·1	35·0
0·002708	89·3	0·571	0·2	51·0	38·3
0·001354	94·0	—	—	—	—
0·001083	95·3	0·550	0·5	52·3	43·0
0·000541	98·2	0·559	1	54·9	43·3
0·0002708	99·3	—	—	—	—
0·0001354	99·9	—	—	—	—

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* MacInnes, Longsworth, and Shedlovsky, 'J. Amer. Chem. Soc.,' vol. 54, p. 2758 (1932).

50·1, and the extrapolation was tested by taking values from the v_R curves in fig. 7, to the left of the last experimental point, subtracting these values from λ at the same concentration, and seeing how the u_{Na} values so obtained fitted the extrapolations. As will be seen from fig. 7, these values fell squarely on the lines drawn.

Table V.—Bordeaux Extra.

Normality.	λ.	T_R	Average deviation.	v_R	u_{Na}
			%		
0·00865	74·5	0·461	0·3	34·3	40·2
0·00650.	76·0	—	—	—	—
0·00606	76·4	—	—	—	—
0·00433	77·7	0·452	0·2	35·1	42·6
0·00325	78·5	—	—	—	—
0·002165	79·9	—	—	—	—
0·001730	80·8	0·434	0·5	35·1	45·7
0·001083	80·9	—	—	—	—
0·000865	81·0	0·416	1	33·7	47·3
0·000433	81·0	—	—	—	—
0·0001083	82·2	—	—	—	—
0	82·$_2$	0·391	—	32·1	50·1

Table VI.—Meta isomer of benzopurpurine 4B.

Normality.	λ.	T_R	Average deviation.	v_R	u_{Na}
			%		
0·0891	51·5	0·681	0·2	35·0	16·5
0·0445	58·2	—	—	—	—
0·02970	62·2	0·668	0·2	41·5	20·7
0·01367	72·1	0·624	0·2	45·0	27·1
0·00802	77·8	—	—	—	—
0·00297	85·4	0·548	0·2	46·8	38·6
0·001604	88·6	—	—	—	—
0·000802	89·4	0·515	0·4	46·0	43·4
0·000401	90·4	—	—	—	—
0·000321	90·1	—	—	—	—
0·0001003	91·4	—	—	—	—
0	92·$_2$	0·446	—	42·1	50·1

III. DISCUSSION OF RESULTS.

A.—*Equivalent Conductivities.*

The curves for equivalent conductivities against square root of concentration, fig. 5, do not become linear in great dilutions, but are distinctly concave downwards. It has been shown in a previous section that this concavity is not due to impurities in the water. The explanation of the concavity becomes obvious from the shapes of the radical equivalent conductivity curves, which are discussed in Section III, C, below.

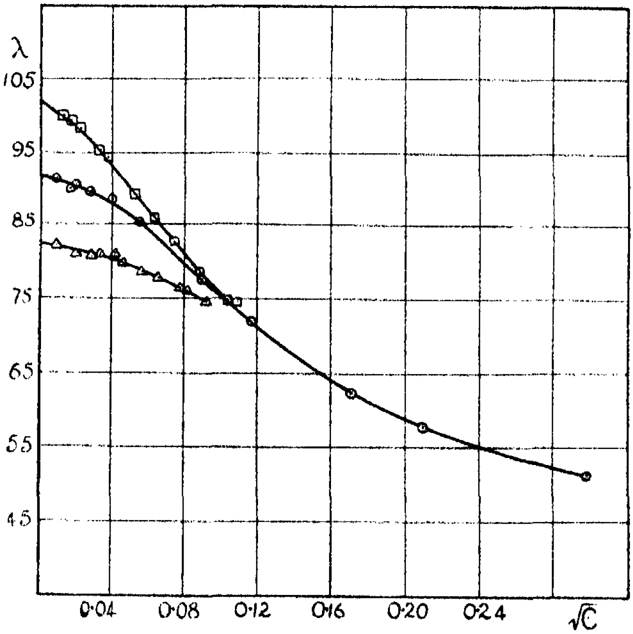

Fig. 5.—□, 4B dye; ⊙, meta dye; △, Bordeaux Extra.

B.—*Transport Numbers.*

The rapid increase with concentration of the transport numbers of the R radicals in these dyes, fig. 6, points to aggregation of the R radicals to form negative micelles, as will be shown.

As McBain* has pointed out, when explaining the minima found by him and his co-workers in the conductivity curves of soap solutions, it follows from Stokes's law that an aggregate of n ions will be $n^{2/3}$ times as mobile as the simple ion. Thus increasing aggregation of the R radical in these dyes will increase the mobility of the R radical as a whole and hence its transport number.

Inclusion of sodium ions by the micelles will, of course, lower their mobility by decreasing their charge. This inclusion will, however, increase the value of T_R. If we first consider only one type of micelles and let f be the fraction of free sodium in the solution, then $(1-f)$ of the sodium will be included by the micelles, and the resultant mobility of the sodium radical will be

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* 'Trans. Faraday Soc.,' vol. 9, p. 99 (1913).

$$U_{Na} = fL_{Na} - (1-f)\,V_R, \tag{6}$$

where L_{Na} is the mobility of the free sodium ions and V_R is the mobility of the micelles. Since V_R is proportional to the net charge on the micelles, which is directly proportional to f, V_R is equal to Kf, where K is a constant. We therefore have

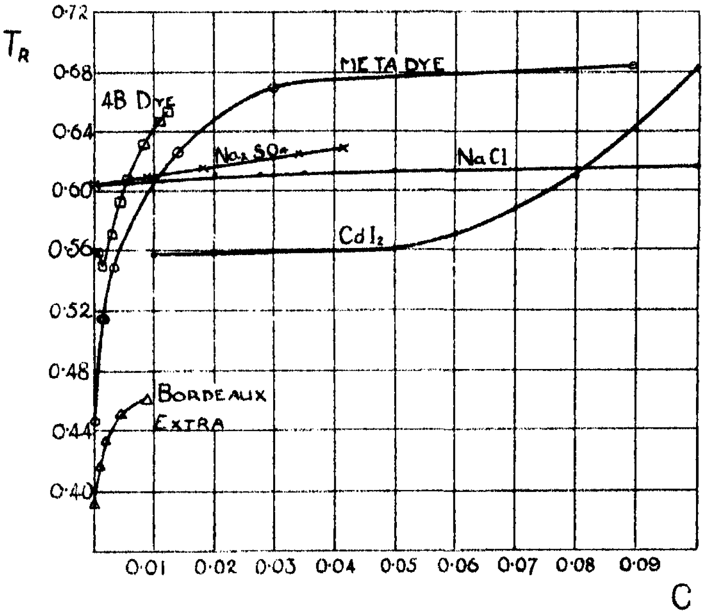

FIG. 6.

$$U_{Na} = fL_{Na} - (1-f)\,Kf, \tag{7}$$

which gives

$$T_R = \frac{K}{L_{Na} + Kf}. \tag{7}$$

From (7) it is apparent that if f decreases (*i.e.*, if more sodium is included), the other factors remaining the same, T_R must increase. The same argument can be extended to include other micellar types. Since increasing aggregation of R and increasing inclusion of Na both increase T_R, the transport number curves can be explained by assuming increasing aggregation of the R radical, with or without increasing inclusion of sodium with increasing concentration. Increasing inclusion of sodium, without increasing aggregation, would, of course, also increase T_R, but this possibility is ruled out in the next section.

These transport number curves are in interesting contrast to those for NaCl,* Na_2SO_4,† and CdI_2,‡ which are included in fig. 6 for comparison. The CdI_2 curve begins to show complex formation only above 0·05 N, whereas the curves for the three dyestuffs point to considerable aggregation in extreme dilutions.

C.—*Radical Equivalent Conductivities.*

Here we have more definite evidence of increasing aggregation with increasing concentration of the meta dye and Bordeaux Extra. The increase in v_R with concentration in the dilute solutions can only be explained by an increase in aggregation, since the other influences act in the opposite direction. Thus increases in the interionic forces and in the amount of included sodium will both reduce the value of v_R. The increase in aggregation is the dominant effect in the more dilute solutions; at higher concentrations the influence of the interionic forces and inclusion of sodium, which reduce v_R, predominates. Where the opposing effects balance, we have a maximum.

The v_R curve for the 4B dye indicates, on the other hand, that the micelles of this dye are more stable than those of the meta dye and Bordeaux Extra. With the possible exception of the changes of the f values with concentration, which are discussed in the next section, we have no proof that the 4B dye micelle breaks down on dilution, since down to 0·0005 N a maximum has not been found. The v_R curve for this dye cannot be completed to zero concentration, because the u_{Na} curve is tending to a zero concentration value of less than 50. Transport number measurements below 0·0005 N would be exceedingly difficult, and perhaps impossible, but it would be of interest to investigate the λ curve at very low concentrations, where a considerable change would be expected.

The fact that the u_{Na} curves for the meta dye and Bordeaux Extra extrapolate to 50·1 furnishes a satisfactory confirmation of the accuracy of the measurements and the purity of the samples of these two dyes. Accidental contaminations in the moving boundary cell would have increased the conductivities of the solutions in the U-tube, slowed down the boundaries, and thus given low v_R and high u_{Na} values. Similarly, any appreciable electrolyte contamination in the samples of the dyestuffs would have given high values for λ and hence high values for u_{Na}.

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* Longsworth, 'J. Amer. Chem. Soc.,' vol. 54, p. 2741 (1932).

† Jahn, 'Z. phys. Chem.,' vol. 58, p. 641 (1907). Measurements by Goldlust.

‡ From Kohlrausch and Holborn's "Leitvermögen," p. 213 (1916).

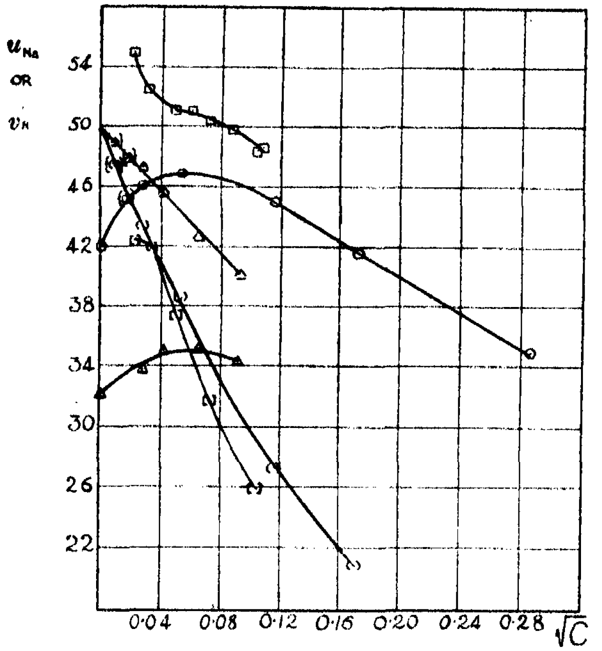

FIG. 7.—□, 4B dye v_R; [ ], 4B dye u_{Na}; ○, meta dye v_R; ( ), meta dye u_{Na}; Δ, Bordeaux Extra v_R; $\underline{\triangle}$, Bordeaux Extra u_{Na}.

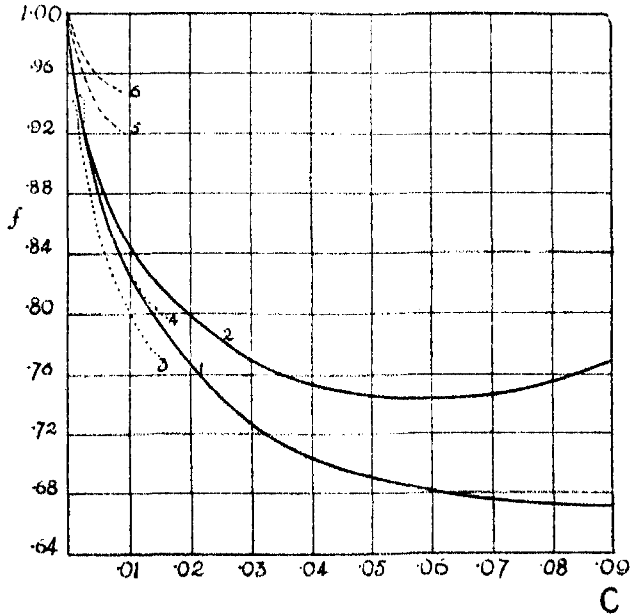

FIG. 8.—1, meta dye on NaCl basis; 2, meta dye on Na_2SO_4 basis; 3, 4B dye on NaC basis; 4, 4B dye on Na_2SO_4 basis; 5, Bordeaux Extra on NaCl basis; 6, Bordeaux Extra on Na_2SO_4 basis.

The u_{Na} curve for the 4B dye seems to be tending to a zero concentration value of less than 50, hence the evidence for the purity of the 4B solution is less conclusive. This effect does not, however, suggest the presence of an impurity, for an impurity would act in the opposite direction.

D.—*Estimation of the Fraction of Free Sodium.*

Equation (6), when multiplied through by the Faraday, can be re-written

$$f = \frac{\lambda}{l_{Na} + v_R}. \tag{8}$$

an expression derived by Hartley and Robinson.*

The actual calculation of numerical values of f from (8) is open to doubt, because values must be assumed for l_{Na}, the equivalent conductivity of the free sodium ions, and in deriving (8) the assumption is made that either (*a*) there is only one type of micelle present, or (*b*) the ratio of Na to R is the same in each of several micellar types. We give in fig. 8, however, the values of f calculated on the assumption that (*a*) or (*b*) is true. This gives fictitious values for f since different types of micelles will exist over at least very short time intervals, but these fictitious values will at least distinguish between considerable and very slight inclusion of sodium. The limited significance of our values should, however, be realized. In one set of curves, l_{Na} is taken equal to u_{Na} in equinormal NaCl solutions; in the other set l_{Na} is taken equal to u_{Na} in equinormal Na_2SO_4, the reasonable assumption being made that NaCl and Na_2SO_4 are practically completely dissociated at the concentrations considered here.

From the curves in fig. 8 it can be concluded that only a small fraction of Na, if any, is included in Bordeaux Extra, but that the meta and 4B dyes contain an appreciable amount of bound sodium.

There is, of course, an alternative explanation for the low u_{Na} values in the meta and 4B dye solutions; that the large interionic forces resulting from the presence of multivalent micelles are sufficient to account for the depression of u_{Na}, without assuming inclusion of Na. Such an explanation, however, meets with the following difficulty. In order to explain the fact that u_{Na} is considerably lower in the meta dye than in Bordeaux Extra, it would be necessary to assume a considerably larger micellar size (*i.e.*, a higher valence type) in the meta dye. This would mean that the ratio of v_R at the maximum to v_R° (v_R at infinite dilution) would be much greater for the meta dye than for Bordeaux Extra, which the curves show not to occur.

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* 'Proc. Roy. Soc.,' A, vol. 134, p. 20 (1931).

E.—*The Mean Effective Micellar Size.*

The mean effective micellar size in these solutions will be defined as the size that would have to be assigned to a single negative micelle, approximately spherical, assuming it to be the only type present, in order to explain the properties of a solution here discussed.

Since v_R^0 in the meta dye and Bordeaux Extra is presumably directly proportional to the velocity of a single R ion in the absence of interionic forces, then from Stokes's law the radical equivalent conductivity v_n of an aggregate of n R's, containing a fraction $(1 - f)$ of the sodium in the solution, will be given by

$$v_n = f v_R^0 n^{2/3} \tag{9}$$

in the absence of interionic forces. If interionic forces could be neglected at N/1000, the value of v_R at that concentration could be substituted for v_n in (9), together with a reasonable value for f, in order to calculate n. Assuming the volume of one R to be the same in the isomeric meta and 4B dyes, v_R^0 would be the same for the two dyes. Table VI contains the results of this calculation for N/1000 solutions of the three dyes.

Table VI.—Mean Effective Micellar Sizes at N/1000.

	v_R^0.	v_n.	f.	n.
Bordeaux Extra	32	34	1·00	1·1
Meta dye	42	46	0·95	1·2
4B dye	42	53	0·94	1·5

In the above calculation the interionic forces have been neglected. In an ordinary electrolyte of low valency their influence could be calculated sufficiently accurately from the Onsager mobility equation. The concentration below which the equation is applicable becomes lower with increasing valency. Until the limits of applicability of this equation have been further investigated for high valence electrolytes, both theoretically and experimentally, we do not feel justified in applying it to such complicated systems as those discussed here.

In the N/1000 solutions the mean effective 4B micelle is definitely larger than the mean effective meta micelle; hence the interionic forces will be greater in the 4B solution. Consequently the value of v_R and therefore of n will have been more depressed in the 4B than in the meta solution. If it were possible to correct for interionic forces, therefore, we should find that not only would the values for n be greater, but the ratio of the n values for the two dyes would be more than 1·5 : 1·2.

Hydration, if appreciable, will have a similar effect in depressing the calculated n values and bringing them too nearly together. Thus the more aggregated micelles, which have the greater charge densities, will be more hydrated, and the hydration lowers v_n in (9) and therefore lowers n.

The values of n given in the table are therefore of qualitative significance. The true values will all be higher, perhaps considerably.

In solutions N/300 or more concentrated, (9) indicates that the 4B mean effective micelle is only slightly larger than that of the meta dye, but distinctly larger than that of Bordeaux Extra. This confirms the interpretation given in the introduction of the osmotic pressure and conductivity results on N/70 solutions of the two benzopurpurines. At this concentration they do not seem to differ greatly in micellar size, but the difference becomes considerable on dilution.

It remains to explain the striking differences in the ultrafilterabilities and flocculation by electrolytes of the two benzopurpurines. The quantitative interpretation of ultrafiltration experiments when dealing with such small particles is known to be difficult. It seems at least possible that the various complicating factors in the ultra-filtration experiments, of which adsorption is only one, have greatly exaggerated the differences between the two dyes. It is intended to deal with both this and the flocculation by electrolytes in a future communication from this laboratory.

Our thanks are due to Professor F. G. Donnan, C.B.E., F.R.S., for the interest with which he has followed this work. We are also indebted to Mr. G. S. Hartley, who has generously given a great deal of time to discussing the problems that have arisen in the course of this research.

Summary.

It is shown how accurate transport number and conductivity measurements can throw light on the states of aggregation of colloidal electrolytes (dyes).

By using the moving boundary apparatus of MacInnes and Brighton, transport numbers of benzopurpurine 4B, its isomer prepared from *m*-tolidine, and Bordeaux Extra, reproducible to one part in five hundred, have been measured over a range of concentrations. From these and concurrent conductivity measurements we are able to conclude that:—

Bordeaux Extra solutions contain negative micelles, more mobile than the simple anions, and practically no sodium is held by these micelles. On dilution the micelles break down gradually into simple ions.

Meta dye solutions contain negative micelles, more mobile than the simple anions. An appreciable fraction of sodium is included in the micelles. On dilution the micelles gradually break down into simple ions.

Benzopurpurine 4B solutions contain negative micelles, more mobile than the simple anions would be, with appreciable amounts of bound sodium. The micelles are more stable than those of the other two dyes, and down to 0·0005 N no proof can be obtained that they are breaking down on dilution.

The number of simple R radicals included in the mean effective micelle of each dye is in the order 4B > meta > Bordeaux Extra. Above 0·003 N the mean effective micelles of the 4B and meta dyes do not differ greatly; below this concentration the 4B micelle is definitely larger.

Progressive Lightning.

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(Communicated by C. V. Boys, F.R.S.—Received October 28, 1933.)

[PLATES 5–8.]

§ 1.

A method of obtaining direct information as to the mode of development of the lightning discharge has been described by Boys.* It consists in the use of a camera with a fixed plate and two lenses revolving in a circle at opposite ends of a diameter. The two pictures of the lightning flash thus obtained show distortions, due to the motions of the lenses, which are in opposite directions. From a comparison of the two pictures and a knowledge of the velocities of the lenses, it is possible to deduce the direction and speed of the developing discharge.

Boys has published† the results of an examination of one such photograph taken by him, in which the discharge began at the ground and almost immediately afterwards started in the length next the cloud. It then travelled from both these parts and finished in the middle portion about 140 microseconds later.

An account has also been given by Halliday‡ of three discharges examined by him with a similar apparatus. Two of these were found to begin at a point above the ground and to travel both upwards and downwards. The third, though it had downwardly directed branches, moved upwards along the main trunk from the ground to the cloud.

The present paper is concerned with the photographs of eleven discharges taken by one of us (H. C.) during the summer of 1933.

§ 2. *The Boys Camera.*

The camera used is one of several placed in the field by the Lightning Investigation Committee of the South African Institute of Electrical Engineers.

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* 'Nature,' vol. 118, p. 749 (1926).

† 'Nature,' vol. 122, p. 310 (1928).

‡ 'Phil. Mag.,' vol. 98, p. 409 (1933).

In designing it we had the advantage of examining Dr. Boys' original instrument which he has very kindly lent to one of us for this work. The two lenses were Zeiss Tessar of 15 cm. focal length and aperture 6·3, specially matched by the makers. They were mounted with their centres 10·1 cm. apart and carried on a ball-bearing axle which was hand-driven at 1500 revs./min. A series of tests showed this rate could always be reproduced to within less than 10%. The photographs were taken on Kodak Super Speed film and measurements were made on unglazed prints. Tests which are described in § 4 showed that no appreciable distortion arose from either the films or the prints, though a small distortion is found to be produced by glazing.

A small fixed camera, rigidly attached to the same stand as the Boys camera, served the important purpose of a view-finder and gave accurate centering of the moving-lens camera on the flashes. The fixed camera pictures have been mounted at the centres of the corresponding Boys' camera pictures.

§ 3. *Method of Measurement.*

In order to compare the two pictures of the same stroke, a line joining corresponding points was ruled across the print with a razor-blade and a good straight edge. The print was then cut up and the two pictures mounted side by side with the two portions of this line parallel to one another. This was made easy by mounting upon squared paper. The instantaneous directions of motion of the lenses were thus made parallel, but opposite and corresponding points on the pictures were placed on the same line of motion. It was usually arranged that the directions of motion were outwards. An example is shown in fig. 1, Plate 8, and another has been published elsewhere.*

The separation between corresponding points on the pictures was measured with a Hilger comparator reading to 1/100 mm. If D and D′ be two such separations and v the relative velocity of the lenses, $(D - D')/v$ gives the time occupied by the discharge in travelling between the two points. Since the relative velocity of the lenses was $1\cdot59 \times 10^3$ cm./sec., a difference of 1 mm. in the separations corresponded to 63 microseconds. This factor, of course, applied to all measurements whether the distortion was along or perpendicular to the path of the discharge.

As the pictures were mounted so that the lens velocities were outwards the measurements of points on either main trunks or branches were made between corresponding points on the inside or nearest edges of the records. Frequently the separation could be measured with an accuracy of less than 2/100 mm. or 1·26 microseconds, but sometimes the presence of glare or the absence of an easily located feature of the track caused the error to rise to 5/100 mm. or 3·2 microseconds. The latter figure is adopted as the possible error in the measurements except where otherwise stated.

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* Schonland and Collens, 'Nature,' vol. 132, p. 407 (1933).

Where approximate results correct to about 1/10 mm. or 7 microseconds were all that was required, a system of lines parallel to one diametral reference line was drawn on the uncut print and the distortions were determined directly with the aid of a glass scale.

Boys (*loc. cit.*, 1928) has also described a very beautiful stereoscopic method of studying the pictures in which they appear in two space dimensions and one time dimension. We have found this of value in suggesting where measurements would be of importance and in filling in the gaps between measurements.

§ 4. *General Description of the Photographs.*

The photographs obtained are reproduced in figs. 2 and 3 and in figs. 4 to 9, Plates 5 to 7, the fixed camera pictures mounted at their centres. The direction of motion of the camera lenses was always clockwise. They can be divided into two sets as follows :—

Figs. 2 and 3, with flashes 1, 2, and 3 on them, were taken on March 2, 1933, from storm No. 1 at a distance of 18 km. This was a large isolated thunderstorm giving usually two or three intercloud discharges before each discharge to earth. Flashes 1 and 2 occurred almost simultaneously.

Figs. 4 to 9, with flashes 4 to 11 on them, were taken on March 30, 1933. The stormcloud (No. 2) was large and isolated, " of triangular shape with the apex towards the ground." There was only a small amount of intercloud discharge and the flashes to earth were frequent and violent. The distance was 9 km. The camera was not correctly trained for flashes 10 and 11, and for flash 11 only one camera lens was able to register. No measurements have been made on these two flashes owing to the possibility of lens distortion of the pictures.

It will be seen that the separate *strokes* constituting a discharge vary in number from one for flashes 3 and 7 to twelve for flash 5. Often these strokes are themselves composite and consist of a faint downward-moving discharge which is followed, when it reaches the ground, by a much more intense upward-moving discharge travelling at a greater velocity. Several good examples are shown by flash 8, fig. 6, Plate 6, but examples occur on every photograph.

These preliminary downward strokes will be referred to as *leader strokes* and the upward strokes which follow them will be called *main strokes*. Though the leader strokes are not always particularly well defined, the combination, as will be seen in the next section, is a very frequent one.

The order in which the strokes are recorded on the clock-wise lens track is not necessarily, or indeed likely to be, that in which they occurred. It is well known that the duration of a complete lightning flash is often a time of the order of 1 second. The camera, however, made one revolution in 0·04 second.*

For ease of reference each stroke has been given a letter, and leader and main components of a stroke are distinguished by the subscripts l and m. Thus $9a_l$ and $9a_m$ signify the leader and the main components respectively of stroke a of flash 9.

In all the flashes observed the separate strokes of a particular discharge appear to follow the same track, the same twists and turns being present on every leader and main stroke.

The presence of continuous circles in figs. 2, 3, 4, and 5 shows that the luminosity persisted along the track for at least one of the strokes during half a revolution, or 0·02 second. The special brightness of the points responsible for these circles arises presumably from the presence of a piece of the track which lies partly end-on to the line of sight. This is true also of some of the streaks which persist for shorter times than the half-revolution required for a circle. Sometimes, however, these streaks are due to the fact that the momentary direction of the lens-motion coincides with the direction of the stroke.

The circles afford a good test of the absence of distortion due to expansion or contraction of either the films or the prints. We can detect no significant departure from true circularity on unglazed prints.

§ 5. *Leader Strokes.*

(*a*) It is of importance to determine whether the leader stroke is a preliminary to all the separate main strokes recorded. Sometimes the leader is so faint that a portion only of the track can be seen. These fainter leaders are associated with flashes where the distortion produced by the lens motion is great, and thus the velocity of the leader small compared with other strokes. Examples are strokes $9c_l$, $8e_l$, and $10a_l$. Where the stroke occurs when the lens movement is approximately vertical and the streaks mentioned in § 4 are prominent, as for strokes 5*a* or 9*g*, the conditions are such that even fairly strong leader strokes could not be detected. Table I contains in column one the list of those strokes which are provided with leaders, while column two contains those which showed none although they would have been visible if of the usual intensity. Column three lists strokes which also showed none, but were so photographed that they would probably not have given detectable leaders unless these were exceptionally strong.

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* This defect of the investigation, which hampers the interpretations in certain directions, has now been rectified by the provision of a slower-moving camera working off the same drive as the Boys' camera.

Table I.—Leader Strokes.

Strokes with leaders.	Strokes without leaders.	Strokes not classifiable.
1 *a*, *b*, *c*		1 *d*
2 *a*		2 *b*, *c*, *d*
		3 *a*
4 *a*, *b*, *d*, *e*	4 *c*, *f*	4 *g*
5 *a*, *d*, *e*, *g*		
5 *h*, *i*, *j*	5 *f*, *b*, *k*, *l*	
		6 *a*, *b*
	7 *a*	
8 *a*, *b*, *d*, *e*, *f*	8 *c*, *g*	8 *h*
9 *a*, *c*, *f*		9 *b*, *d*, *g*
10 *a*	10 *b*	
11 *a*, *c*		
Numbers 26	10	14

Two strokes included in the first column require special comment: 5*d* is preceded by a downward leader-like stroke, 5*c*, the end of which is not visible on the record. This may have hit the ground a short time before 5*d* began, as certainly happened with 9*f* which is preceded by the downward stroke, 9*e*, 0·0011 second before. These two downward strokes, 5*c* and 9*e*, are the only downward discharges which are not followed instantaneously by upward strokes. It is quite possible that 5*c* is normal in character, and joins up with the base of 5*d*.

The table shows that the proportion of strokes with leaders is 26/36 or 72%. We consider this to be an understatement, for some of the strokes in the second column, such as 5*b*, *k*, *f*, and *l*, might reasonably have been included in the third.

We have been privileged to examine another photograph, taken with a Boys' camera by Dr. Halliday, on which four out of five strokes show leaders, the fifth stroke being unclassifiable. If we include this result, the percentage of strokes showing leaders is at least 75% of the 40 strokes which we consider can be classified. The existence of leader strokes has been demonstrated for three different thunderstorms and for ten out of twelve distinct lightning flashes.

It seems possible, therefore, that only the exceptional strokes forming part of these lightning flashes fail to be preceded by visible leaders from cloud to ground. Of the ten leaderless strokes of Table I, four (*4f*, *5l*, *7a*, and *10b*) are exceptional in being heavily branched. Two others (*8c* and *8g*) have upward strokes immediately preceding them, and with these they are undoubtedly associated.

(*b*) *The Velocities of the Leader Strokes.*—The values found for the velocities of those leader strokes, which are sufficiently clear over some distance to be measured, are given in Table II. The points chosen for measurement were the two ends at cloud and ground and the velocities are given both along the straight line joining these ends, column 2, and along the tortuous two-dimensional track, column 3.

Table II.—Velocities of Leader Strokes.

Stroke.	Straight line velocity. cm./sec. $\times 10^{-8}$.	Track velocity. cm./sec. $\times 10^{-8}$.
1b	2·3	4·8
1c	2·3	4·8
2a	3·4	4·0
4a	1·1	1·3
4b	10·0	11·1
4d	1·6	1·8
4e	14·5	16·1
5d	3·9	4·8
5e	4·3	4·8
5g	5·5	6·3
5h	2·0	2·3
5j	8·5	9·7
8a	12·0	14·4
8b	13·3	15·5
8d	7·2	8·3
8e	6·3	7·2
8f	4·3	5·1
9a	6·0	7·0
9c	1·1	1·4
9f	27·1	32·1
Means	7·0 $\times 10^8$ cm./sec.	8·3 $\times 10^8$ cm./sec.

Note.—The majority of these measurements were made by the rough method described previously. The order of accuracy is 10%.

The lengths involved in these measurements range from 1·0 to 2·9 km. measured along the two-dimensional track picture. The longest time occupied in the passage from cloud to ground was found for stroke $9c_l$ which took 1670 microseconds to do 2·3 km. The quickest leader, stroke $9f_l$, took 69 microseconds to do 2·2 km.

Mean values for the velocities are shown in the last line of Table II. The maximum and minimum values for the straight line or vertical velocities are $2 \cdot 7 \times 10^9$ and $1 \cdot 1 \times 10^8$ cm./sec. respectively. The corresponding track velocities are $3 \cdot 2 \times 10^9$ and $1 \cdot 3 \times 10^8$ cm./sec. As will be shown in the next section, parts of certain tracks show velocities smaller than these minimum values.

The values given for the track velocities refer to the track projections and are therefore too small. For these flashes the ratio of projected track length to direct distance between the ends varies from 1·1 to 2·1, with an average of 1·3. We shall therefore not be far wrong in increasing the tabulated track velocities by 30% to obtain the actual velocities along the tortuous three-dimensional track. The true minimum, mean, and maximum track velocities are then of the order of $1 \cdot 7 \times 10^8$, $1 \cdot 1 \times 10^9$, and $4 \cdot 2 \times 10^9$ cm./sec.

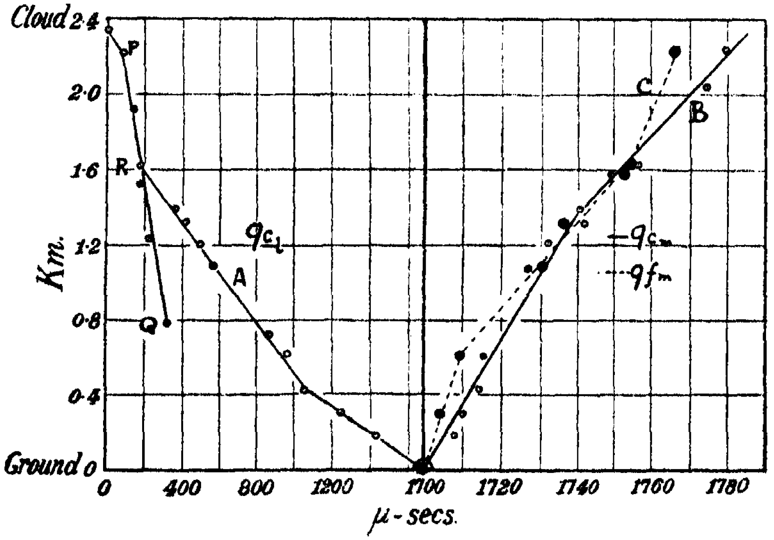

FIG. 2.

(c) *Some detailed Measurements on Leader Strokes. Stroke* $9c_l$.—This particular leader stroke is shown in fig. 9, Plate 7. It is exceptionally slow and much distorted by the movement of the lenses. It is of special interest because it is the only leader which shows a branch. It begins with the production of this branch track, which terminates in the air after traversing only about one-third of the vertical distance between cloud and ground. After this branch has reached its end, a second track develops from a point half-way down the first and travels to the ground. The measurements on this leader are shown in the left-hand compartment of fig. 2. Ordinates are the distance along the two-dimensional tortuous track measured from the ground up. Abscissæ are the time in microseconds measured from the start of the first branch from the cloud. This first track, PRQ, travels at a constant velocity of 5·5 × 10^8 cm./sec. The second, marked A in the figure, moves at 1·2 × 10^8 cm./sec, for 1·2 km. after the branching point and then slows down. The last 400 metres of its journey show the slowest speed so far observed for any part of a leader stroke, 6·7 × 10^7 cm./sec.

The stroke affords a good example of the variation in intensity of the leader with velocity, PRQ, which is the fastest portion, being clearly defined while the lower end of A is barely visible.*

Stroke $8d_l$.—This leader stroke is shown in fig. 8, Plate 7, and the measurements on it are represented graphically in fig. 3. Like the previous leader it progresses with three speeds, travelling for the first 0·7 km. of its path at 9·3 × 10^8 cm./sec. and for the last 600 metres at 5·3 × 10^8 cm./sec.

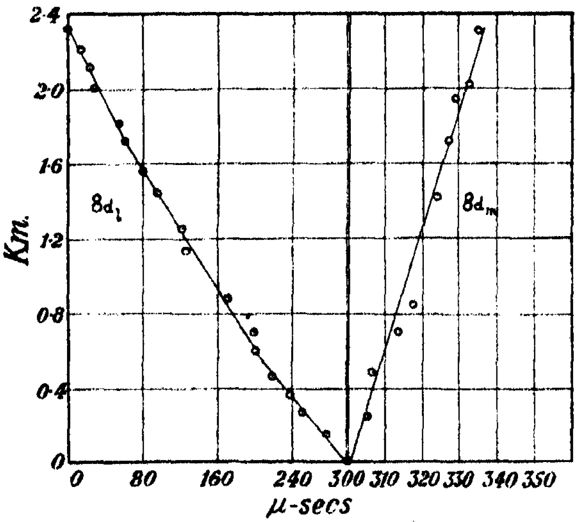

FIG. 3.

(*d*) *The Width and Nature of the Leader Strokes.*—An important feature of the leader strokes is that their tracks appear to preserve a constant width. It follows that, as Boys pointed out for the flash photographed by him, the stroke is propagated as a limited region of luminosity in the manner of an elongated fireball or dart. The width of the actual track itself would, of course, not be measurable on the reduced photograph. The observed width is due to two factors: the finite width of the image formed by the photographic lens and emulsion and the effect of the continuance of luminosity at points along the track. This last, combined with the motion of the lens, causes the image of the track to be dragged out into a band.

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* In order to show this part of the leader it has been necessary to reproduce this photograph, fig. 9, from a glazed print.

Consideration of the second factor by itself enables one to place an upper limit to the length of the dart. For a dart of length l moving with a velocity V would give rise to a luminosity enduring at each point for l/V seconds and the track would be drawn out into a band of width lv/V cm. if v is the velocity of the camera lens. Values found for the upper limits of l are shown in Table III.

Table III.—Maximum Lengths of Leader " Darts."

Stroke.	l (metres).
$4b_l$	52
$4e_l$	40
$5j_l$	48
$8a_l$	112
$8b_l$	96
$8d_l$	40
$8f_l$	25
$9c_l$ (PRQ)*	28
$9c_l$ (A)*	43
Mean	54

* Fig. 2.

Although the leader tracks are formed by the movement of an agent, here called a dart, which gives strong luminosity along a limited region, the photographs show that all the tracks remain faintly luminous after the main dart has passed by. A faint spreading of the track continues without observable break, in the direction of the lens motion. Strokes $8b_l$ and $9c_l$ are examples. For the slowest and faintest tracks the actual dart track is so weak and narrow that it can barely be distinguished from the edge of this region. In the majority of strokes there is, of course, no question as to the reality of the actual track which precedes this faint continuous luminosity.

§ 6. *The Main Upward Strokes.*

(*a*) The main strokes which follow the leaders are obviously of a different character, being thicker, more intense, and of decreasing thickness in the upward direction. Measurement shows that all the 39 strokes of this kind

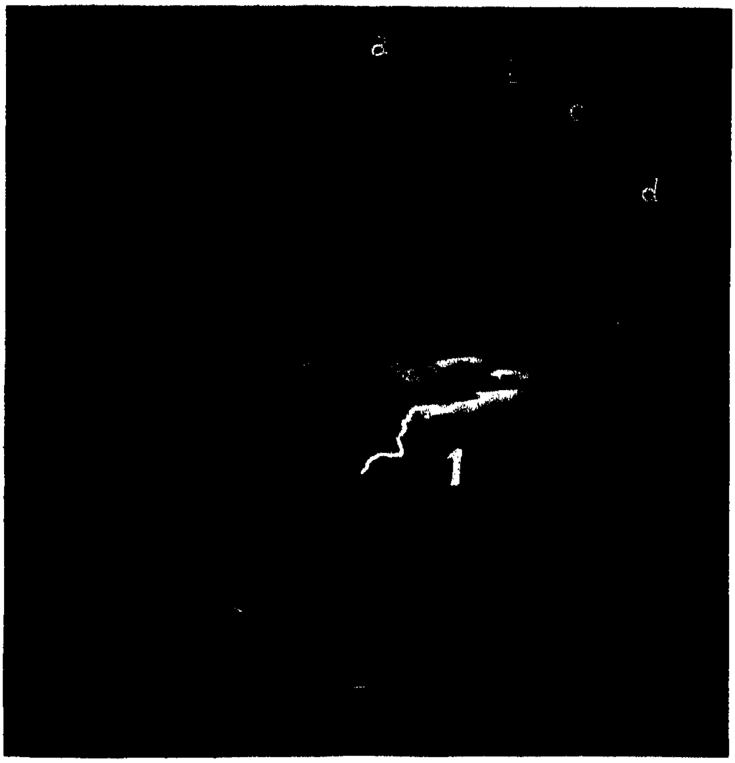

Fig. 4.

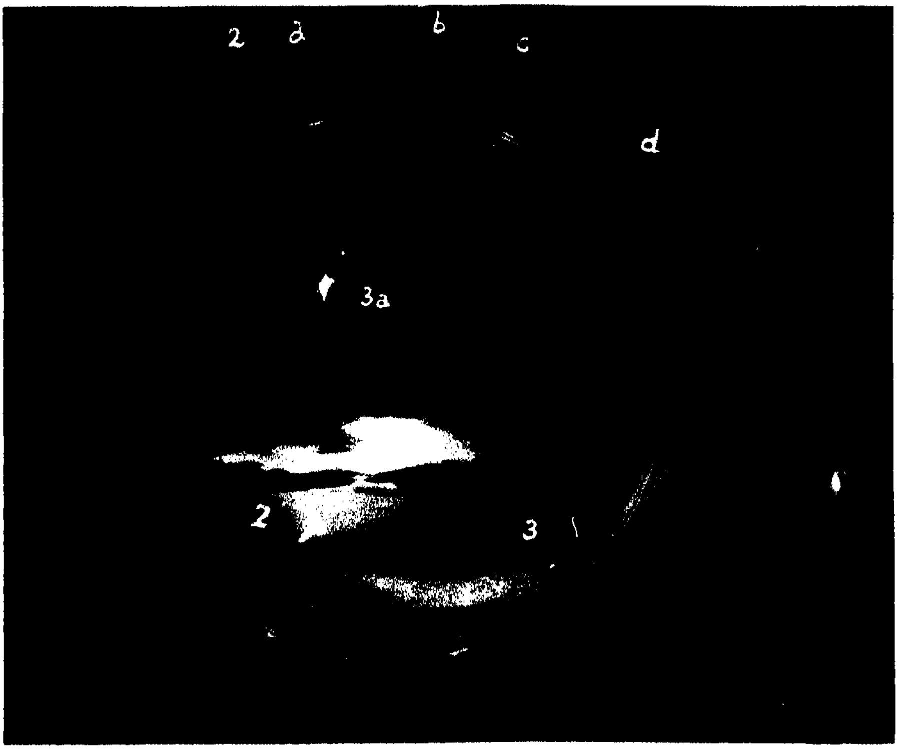

Fig. 5.

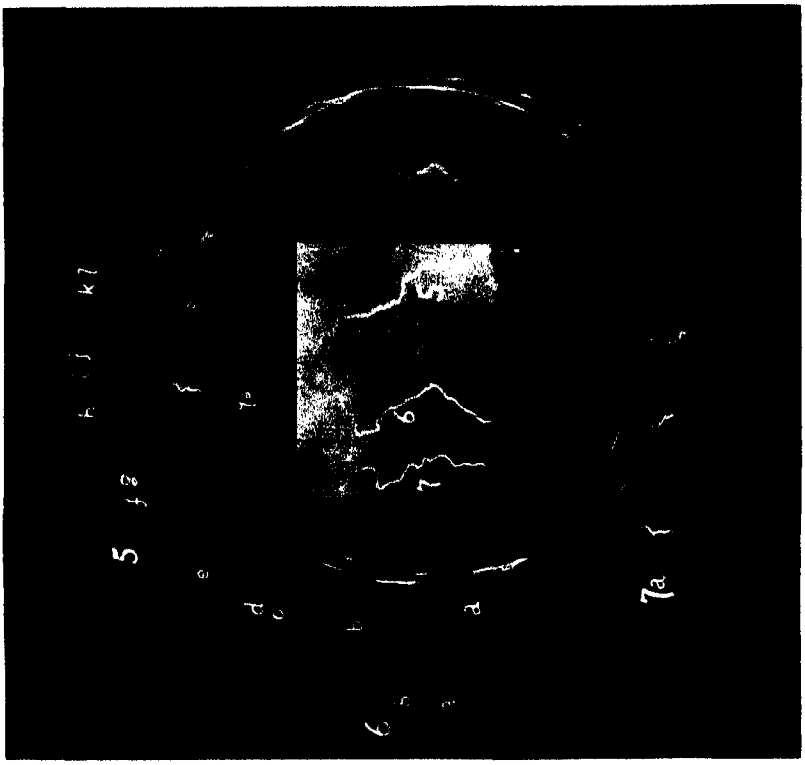

Fig. 7.

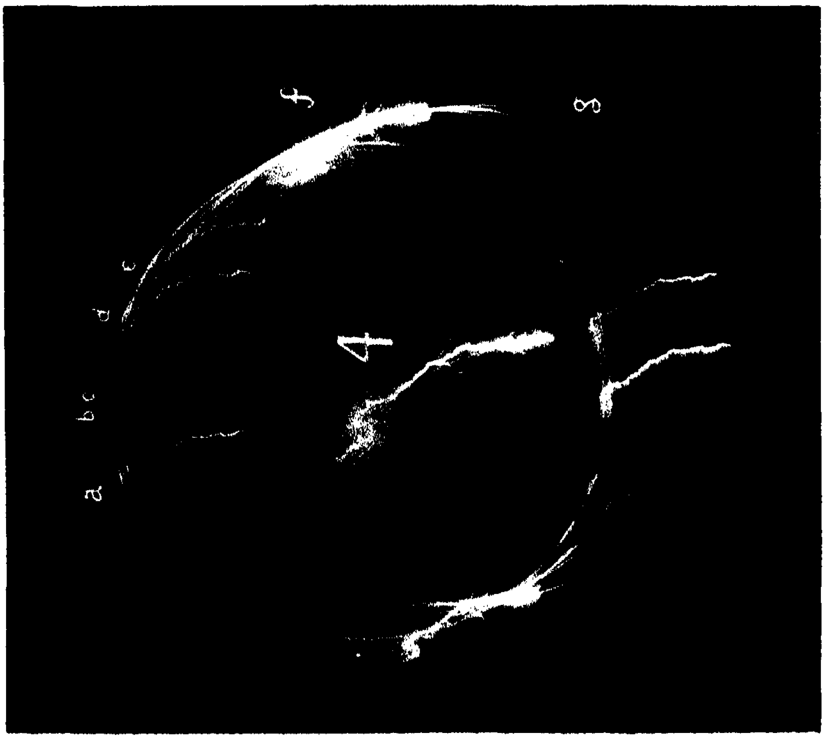

Fig. 6.

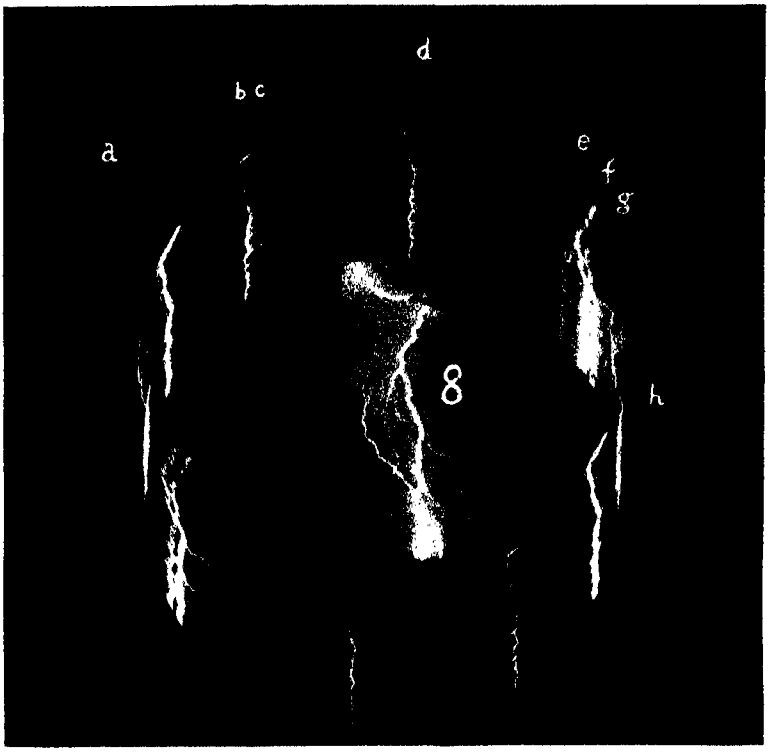

Fig. 8.

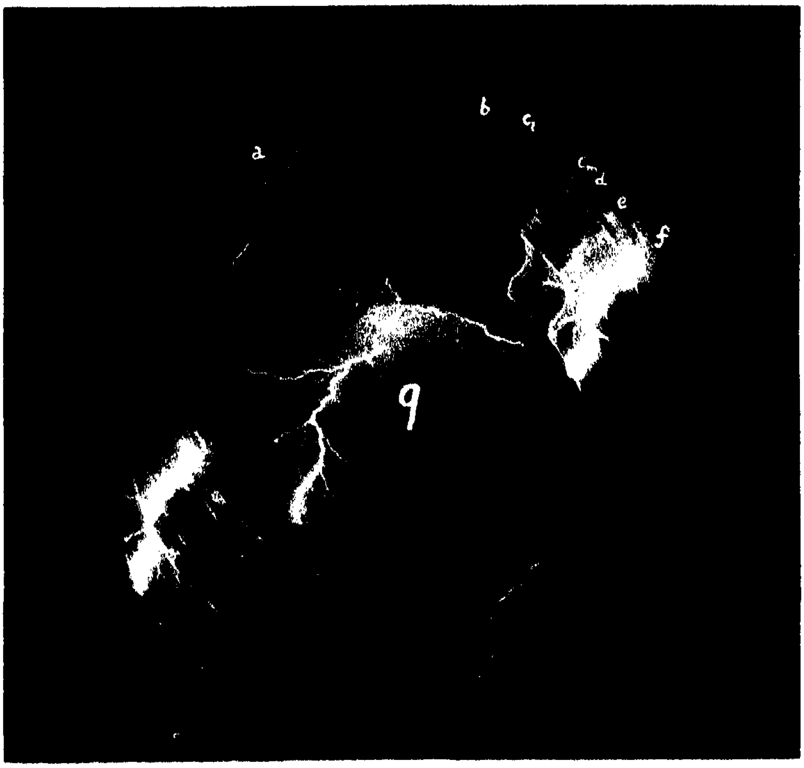

Fig. 9.

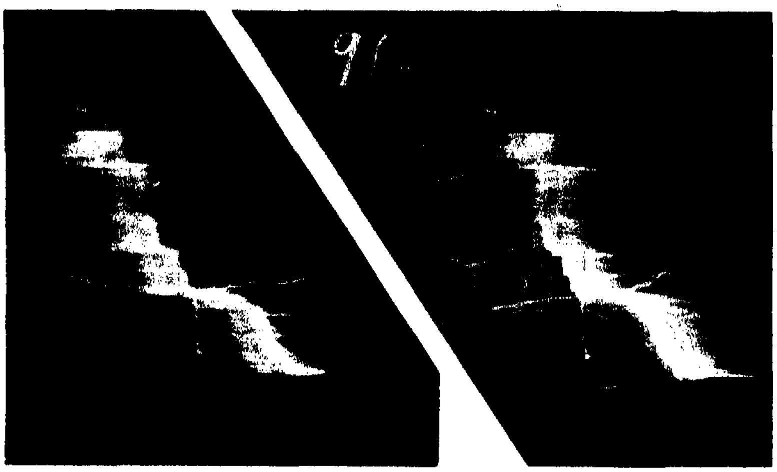

Fig. 1.

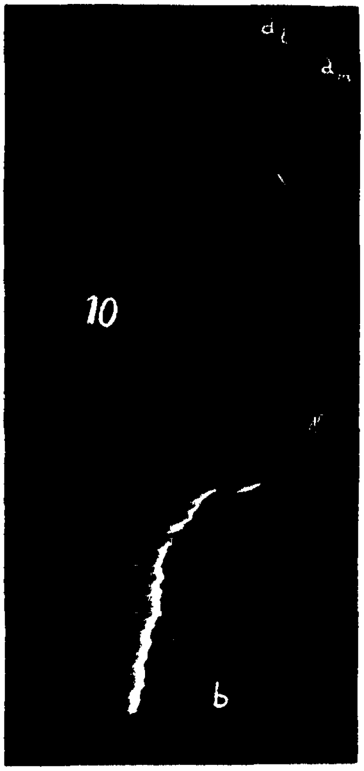

Fig. 10.

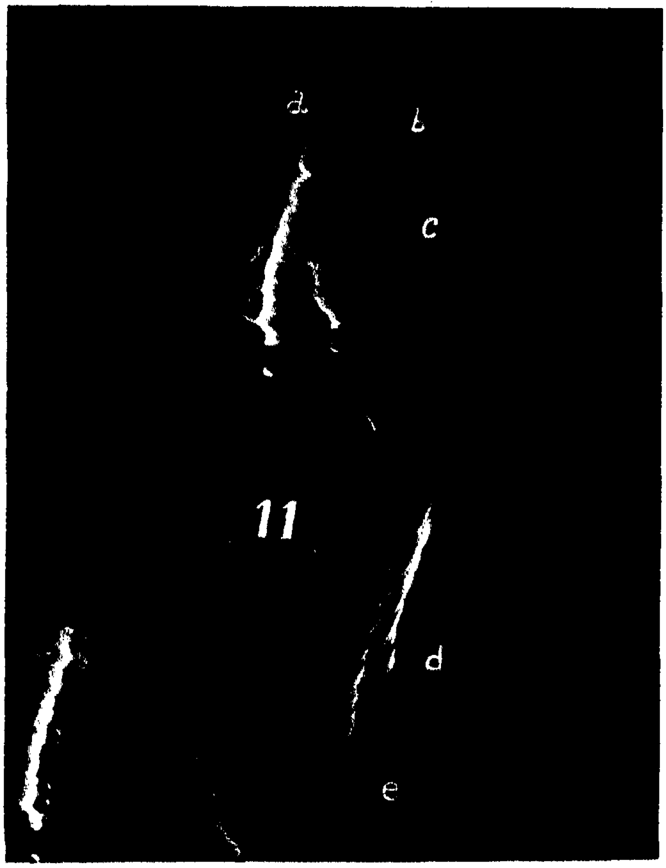

Fig. 11.

included in flashes 1 to 9 which can be measured travel in the direction from ground to cloud. Flash 10, Plate 8, shows the same, but can hardly be included owing to possible lens distortion, and flash 11, Plate 8, cannot be examined on this point.

(*b*) *Velocities of Main Strokes.*—The results of measurements of the mean ground to cloud velocities of these strokes are shown in Table IV. The mean straight line, end-to-end, velocities have an average value of $3 \cdot 84 \times 10^9$ cm./sec., while the two-dimensional track velocities average $4 \cdot 6 \times 10^9$ cm./sec. The corresponding minimum values are $1 \cdot 3 \times 10^9$ (st. line) and $2 \cdot 4 \times 10^9$ cm./sec. (track). The maximum values are $7 \cdot 4 \times 10^9$ (st. line) and $11 \cdot 0 \times 10^9$ cm./sec. (track). As already explained, the track velocities along the actual three-dimensional discharge may be expected to be 30% greater.

Table IV.—Velocities of Main Upward Strokes.

Stroke.	Straight line velocity. cm./sec. $\times 10^{-9}$.	Track velocity. cm./sec. $\times 10^{-9}$.
1*b*	5·4	11·0
1*c*	3·3	7·0
1*d*	1·3	2·4
2*a*	6·5	7·7
2*c*	4·7	5·5
4*a*	7·4	8·8
4*b*	5·4	6·5
4*c*	3·2	3·9
4*d*	6·4	7·8
4*e*	8·3	10·0
4*f*	4·0	4·8
5*a*	5·4	6·8
5*b*	3·9	2·1
5*d*	4·3	4·8
5*e*	3·6	4·1
5*f*	3·1	3·5
5*g*	4·4	5·0
5*h*	2·6	3·0
5*i*	2·1	2·4
5*j*	2·6	3·0
5*k*	2·4	2·7
5*l*	3·2	3·6
6*a*	2·4	3·1
6*b*	1·9	2·5
7*a*	2·5	3·3
8*a*	3·2	3·7
8*b*	3·0	3·5
8*c*	2·9	3·3
8*d*	5·7	3·5
8*e*	2·9	3·3
8*f*	2·1	2·4
8*g*	3·4	3·9
9*a*	2·5	3·1
9*b*	3·1	4·3
9*c*	2·4	2·8
9*f*	2·8	4·2

(*c*) *Special Measurements. Stroke* $9c_m$.—Measurements along the track of this stroke, which followed immediately upon the arrival of the leader at the ground, are shown in the right-hand compartment of fig. 2, curve B. The time continues to be measured from the start of the leader stroke, but the time-scale has been altered to allow for the greater velocity of the main stroke. The velocity of $9c_m$ appears to decrease after the first 1·2 km. have been traversed, but it must be remembered that this is the velocity along the projection of the track upon the plane of the photographic film.

This stroke shows a faint branch to the left corresponding exactly in position and shape with the branch on the downward leader described in § 5 (*d*). The branch does not appear on any other stroke except $9f_m$ (branch 1, fig. 15) and there it is not completely reproduced.

Stroke $9f_m$.—This stroke, with others which are heavily branched, is discussed in the following section. The progress of its main channel is, however, shown in fig. 2 as curve C for comparison with that of $9c_m$. The two strokes are surprisingly similar in their rates of movement, though at its beginning and at its end $9f_m$ moves faster than $9c_m$.

Stroke $8d_m$.—The time-table for this track, which follows the leader discussed previously, is shown in the right-hand compartment of fig. 3. The velocity appears to be constant throughout its progress.

None of these upward-moving strokes show any evidence of pauses during their passage. The same result is found to hold for the heavily branched tracks examined in the next section.

(*d*) *The Width of the Main Stroke Channels.*—The main strokes, like the leaders, are pulled out by the camera motion to a width which depends, at least in part, upon the duration of the luminosity at each point. The record of the channel again takes two forms, the bright track being succeeded by a less luminous one in which certain points show up brighter than the rest. These two types of luminosity will be distinguished as bright and glow luminosity.

The bright channels differ from those of the leaders in not being of uniform thickness throughout their length. The bright luminosity in the lower parts continues for a longer time than that higher up, showing that the base of the channel remains bright for part at least of the time occupied by the upward passage of the stroke. The mode of development of the main strokes therefore resembles that of a flame rather than a dart. The bright base does not, however, continue for the whole time occupied in the passage. Measurements on 22 strokes give values for the duration of bright luminosity at the base which range from 0·2 ($8c_m$) to 0·7 ($4a_m$) times the time taken by the stroke to pass from ground to cloud. The thick branched flashes to be discussed later are not included in this list.

The glow luminosity which follows the bright channel lasts for a much longer time. Thus the base of the discharge is bright until the upward-moving tongue has travelled about half the distance between ground and cloud and then changes to the weaker glow which lasts long after the tongue has reached the cloud.

§ 7. *Branched Main Strokes.*

The majority of the main strokes show no signs of branching and sometimes only one stroke in the series which constitutes a single discharge is branched. Exceptions are flash 9 with a heavily branched stroke f and a faintly branched stroke c (§ 6 (c)) and flash 8 which has branches on strokes a, e, f, and g. Flashes 3 and 7, on the other hand, each consist of a single branched stroke only.

Four of the heavily branched strokes are clear enough for measurement and time-tables for these are shown in figs. 12 to 15. The numbers attached to the various points are the times in microseconds at which they were first registered by the camera and the zero of the time scale is the first record of luminosity at the base of the stroke. Some of the branches have been numbered. The points chosen for measurement were those which possessed clearly defined characteristics. The time values shown have usually been remeasured several times with different sets of prints and have been found to be reproducible to within 3 microseconds. No reliable measurements can be made upon the main trunk of stroke $4f_m$, fig. 12, owing to the presence of glare.

(*a*) *The Direction of Development of the Branches.*—The figures show clearly that there has been no record of the development of branches otherwise than outwards from the main trunk. Those branches which are best suited for measurement, such as $9f_m$ branch l and $8f_m$ branch 4, show the outward growth of the branches very clearly.

(*b*) *Times of Starting of the Branches.*—The branches appear to start outwards from the trunk either at the moment of arrival of the discharge at the branching-point or later. Often the start of the branch may be much delayed. On $8f_m$ (branch 2) and $4f_m$ (branch 1) there are examples of branches which seem to have started out after the main channel had passed well by and had practically reached the base of the cloud. There is no evidence for the starting of any part of a branch before the arrival of the main channel at the branching point.

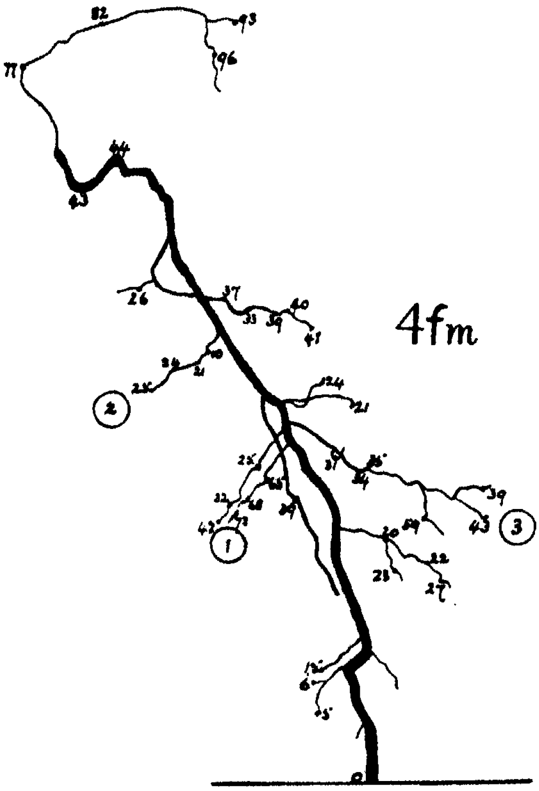
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Fig. 12.

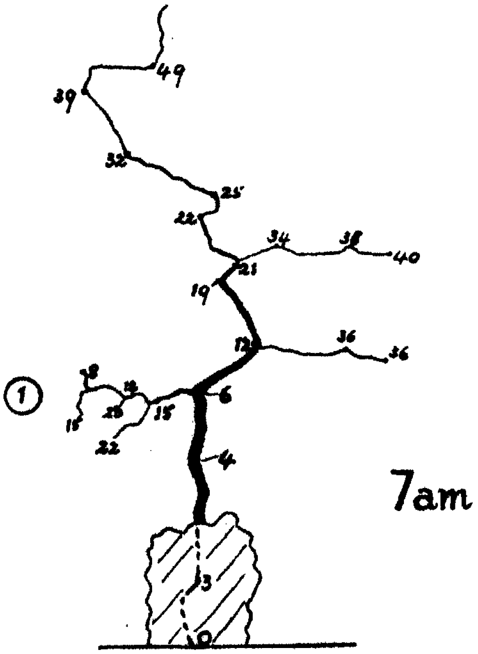
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Fig. 13.

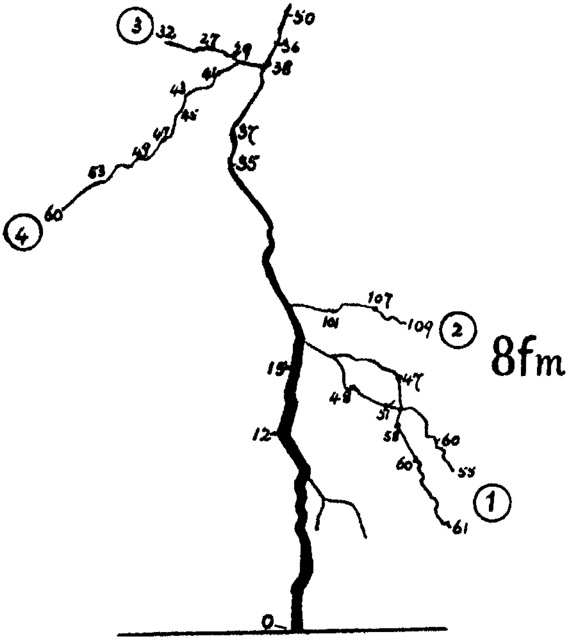
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FIG. 14.

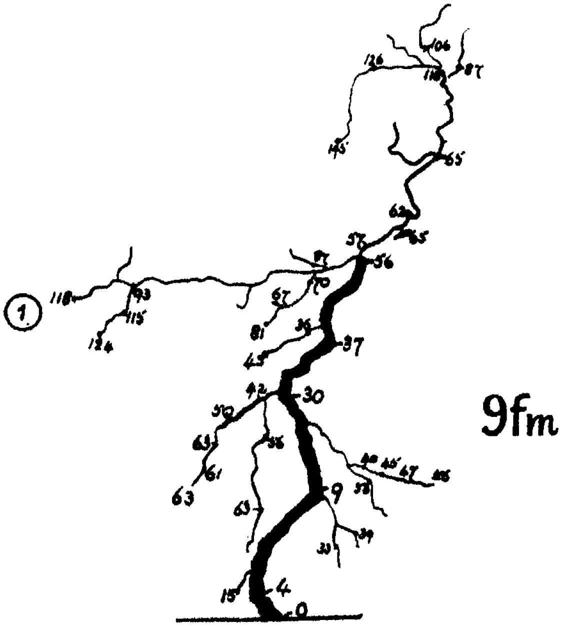
①
9fm

FIG. 15.

In general the branches do not develop from the main trunk in a regular sequence with the lowest branch first and the highest last. On $8f_m$, for example, branch 4 is contemporaneous with branch 1 and both are much earlier than branch 2. On $4f_m$ branch 2 is very early, though half-way up the channel and branch 1 is very late. The timing of these branches is confirmed and well shown by the stereoscopic method.

(*c*) *The Velocities along Branches.*—The velocity of growth of the luminous channel along a branch has been determined for some of the longer branches. The results are shown in Table V.

Table V.—Rate of Development of Branches.

Stroke.	Branch.	Length measured. (km.)	Time. (microsecs.)	Velocity. (cm./sec. × 10^{-9}.)
$8f_m$	1	0·45	14	3·2
$8f_m$	4	0·6	20	3·0
$9f_m$	1	1·05	46	2·3
$4f_m$	3	0·95	19	5·0

Comparison with Table IV shows that the branches develop at a rate similar to that of the main trunk.

(*d*) *The Duration of Luminosity in the Main Channel.*—A comparison of the duration of the strong luminosity at the base of the discharge channel with the time required to trace out the distance between ground and cloud and to develop the last branch is of interest. The measurements, which owing to glare and the presence of the glow luminosity can only be approximate, are shown in Table VI.

Table VI.—Duration of Luminosity in Main Discharge.

Stroke.	Duration at base* (bright luminosity). (microsecs.)	Time required to reach cloud. (microsecs.)	Time required to reach end of last branch. (microsecs.)
$4f_m$	125	44	96
$8f_m$	162	50	61
$9f_m$	150	65	145
$7a_m$	12	49	40

* As in § 5 (*d*) these are upper limits to the duration.

For the first three strokes the duration at the base corresponds to a time greater than that required to trace out the channel for the main trunk, which means that the discharge continues after the channel has been blazed. Stroke *7a*, however, is a striking exception, for its main channel only keeps brilliantly luminous for a quarter of the time required for the passage of the discharge from ground to cloud.

In showing this behaviour stroke *7a* affords an extreme illustration of an effect which is common to the majority of the branched strokes, the main channels of which are generally found to decrease in thickness with each branch that is formed and to lose their intense luminosity altogether after the last branch has been reached. Stroke *7a* concentrates most of its intensity upon the first branch up from the ground, becomes weaker after the second and changes to glow luminosity after the third and last branch. The same behaviour is shown by stroke $9f_m$, figs. 1, 15, which very clearly loses its thick channel after the last branch has been formed. Stroke *5l*, whose main branch occurs near the bottom and just above a fringe of trees, does the same, though it continues to produce a much diminished channel until it reaches its second and last branch near the cloud-base. Other examples are afforded by $8f_m$ and $10b_m$. Stroke $4f_m$ is the only exception and in this the last branch is produced at the very end of the channel.

The width of the main channel at any point is a measure of the time during which it remained strongly luminous after the discharge first reached it. The sudden discontinuities just noted indicate that the activity which makes the channel brightly luminous is engaged primarily in pouring energy into the branches and not in providing a discharge between ground and cloud. Thus the bright channel which ends at the start of branch 1 of $9f_m$, fig. 15, actually remains luminous there for between 60 and 100 microseconds, feeding energy into the branch the end of which is attained at something more than 68 microseconds after the start. Similarly at branch 1 of $7a_m$ the bright channel has a duration of 12 microseconds, corresponding to the 14–16 microseconds required for the full development of the branch.

The most obvious manner in which these changes in the width of the channel could occur would be for the discharge to pause at each branch to pour energy into it. We can find, however, no evidence of such pauses at branching points in the main channel. On the contrary, the main channel appears to go smoothly on past these points. The transitions from bright to glow luminosity along the tracks shown in figs. 15 and 13, for example, seem to involve no pauses in the development of the upward-moving channel.

§ 8. *Discussion.*

The results described in the preceding sections will, we hope, be supplemented before long by many more. The experience gained in this investigation has led to the adoption of certain improvements in operating which should clear up some of the doubtful points and enable others to be examined. In view of this it is intended to defer a detailed discussion of the present results and their consequences until further material is available and to direct attention here to a few points which appear to be beyond question.

(*a*) *The Leader Strokes.*—Downward moving, dart-like, leader strokes seem to be a necessary preliminary to practically all the main strokes examined. It appears that the only interpretation which can be placed upon them is that they are electron avalanches or darts of the kind suggested by Dorsey* for the lightning discharge and by Rogowski,† Slepian,‡ von Hippel§ and others as a preliminary to the spark discharge between metal electrodes. There is general agreement that in the spark the passage from cathode to anode of a primary electron, ionizing by collision and consequently soon accompanied by a host of others, is a necessary preliminary to breakdown. Direct evidence for this appears so far, however, to have been lacking.

This interpretation would require the polarity for the nine discharges whose strokes show leaders to be such that the base of the cloud is negative and the ground positive. This is in agreement with investigations on cloud polarity and cloud-ground discharges by the author‖ and by Halliday¶ as well as with those of workers in other countries.** Further confirmation of the correctness of this explanation of the nature of the leader strokes can be obtained from a comparison of their velocities with those to be expected of an electron avalanche.

An electron in air at N.T.P. has a mean free path of about $5 \cdot 4 \times 10^{-5}$ cm. In a field of the usual critical strength of 30 kv./cm. it would acquire an average velocity between collisions of $4 \cdot 4 \times 10^{7}$ cm./sec. Since the ionization potential for air is about 16 volts and the average energy of the electron just before a collision would be $2\frac{1}{2}$ volts, only exceptionally long free paths could cause ionization and most of the collisions would be elastic or produce excitation without ionization. Experiment, however, indicates that in such a field about 20 collisions per centimetre involve ionization. This number (Townsend's constant α) falls off rapidly with velocity and becomes negligible for fields of strength less than 20 kv./cm. in which the velocities of the electron and its products are less than $3 \cdot 6 \times 10^7$ cm./sec.

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* 'J. Franklin Inst.,' vol. 201, p. 485 (1926).

† 'Sommerfeld Festschrift,' 1929.

‡ 'Elect. World,' vol. 91, p. 761 (1928).

§ 'Z. Physik,' vol. 80, p. 19 (1933).

‖ Schonland, 'Proc. Roy. Soc.,' A, vol. 118, p. 233 (1928).

¶ *Ibid.*, vol. 138, p. 205 (1932).

** Watson-Watt, 'J. Roy. Met. Soc.,' vol. 57, p. 133 (1931).

In the present work the mean pressure of the air at the middle of the discharge channel is about 54 cm. Hg so that the value of α would be negligible, and avalanches could not be formed, at velocities less than $3 \cdot 0 \times 10^7$ cm./sec. This should represent the lower limit to the velocity of a leader flash if it consists of an electron avalanche, and is in satisfactory agreement with the value $6 \cdot 7 \times 10^7$ cm./sec. found in § 5 (*d*) for the velocity of the slowest part of the slowest leader stroke recorded.

With increasing velocity the value of α increases rapidly, becoming about 140 at $5 \cdot 8 \times 10^7$ cm./sec. and reaching a maximum of 4000 ions/cm. at about 4×10^8 cm./sec. Thereafter it decreases slowly and has fallen to 400 at $1 \cdot 0 \times 10^{10}$ cm./sec.

The rapid rise to a maximum is in accord with the changes in the intensity of the leader strokes with velocity noted in § 5 (*d*). The most intense leaders have velocities ranging from 4×10^8 to 13×10^8 cm./sec., corresponding satisfactorily with the broad maximum of α which begins at 4×10^8 cm./sec. The fastest leader observed has a velocity of $2 \cdot 7 \times 10^9$ cm./sec., for which α is still 1700.

The mechanism of propagation of the dart-like avalanche at these high velocities will not be discussed here. Dorsey's view (*loc. cit.*) that such darts constitute the whole lightning stroke is evidently not supported by these flashes, for it is only on the arrival of the leader at the ground that the main breakdown occurs.

(*b*) *The Main Strokes.*—The main strokes in general follow immediately upon the arrival of the electron avalanches at the ground and always travel from ground to cloud, *i.e.*, from anode to cathode. Their appearance and character suggests that the bright channels are thermally ionized,[*] the intense field at the tip of the discharge causing electrons (and possibly positive ions as well) in front of the tip to acquire velocities sufficient to raise the gas to a high temperature by cumulative ionization and by excitation.[†] The interesting fact that the channels follow in every detail the track previously blazed by the downward leader indicates that the main stroke requires a pre-existing and plentiful supply of ions for its rapid development.

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[*] Slepian, *loc. cit.*; v. Hippel, *loc. cit.*

[†] Simpson, 'Proc. Roy. Soc.,' A, vol. 111, p. 56 (1926).

In these observations the values found for the ratio of the velocity in the field direction to that of light range from 0·05 to 0·25, with a mean of 0·12. Values for the duration of the discharge found by Peek* (< 5 μ secs. for discharges 500 metres long) give velocities of the same order. Rudenberg has given theoretical reasons for anticipating that this ratio cannot exceed a fraction of the order of 0·25.†

For the laboratory spark, measurements of the velocity of the anode to cathode discharge have been made by Holzer‡ and others. For a maximum electrode separation of 12 cm. Holzer found a velocity of $6 \cdot 6 \times 10^8$ cm./sec. (0·05 c.). The velocity was observed to increase with the distance between the electrodes.

The need for a preliminary cloud to ground leader before breakdown can take place offers a satisfactory explanation of the fact that one of us (B. S.) has twice observed that very small fields prevailed at the ground immediately before most unexpected discharges to earth at distances of less than 400 metres from the point of observation.§

(*c*) *The Branched Discharges.*—The observations here described support the discovery of Halliday‖ that upward moving strokes develop branches which are sloped downward or away from the cloud. In one instance at least a satisfactory interpretation is available; stroke $9c_m$ develops such a branch because the trail for it was blazed by the leader just before. There is, however, no other record visible on these photographs of a branching leader and the adoption of this interpretation for branches in general must await further direct evidence.

Branching into the air from the anode is a well-known phenomenon and was interpreted by Simpson (*loc. cit.*) in his well-known memoir on lightning. The same explanation could be applied here, with the earth instead of the thundercloud base as anode. The branches should then, however, be directed upwards and not downwards. It has been shown by Allibone¶ and one of us that excellent branching can also be produced from the cathode of the laboratory

* 'Trans. Amer. Inst. Elect. Eng.,' vol. 50, p. 1077 (1931).

† 'Wiss. Veröff. Siemens-Konzerns,' vol. 9, p. 1 (1930).

‡ 'Z. Physik,' vol. 77, p. 677 (1932).

§ Schonland, 'Trans. S. Afr. Inst. Elect. Eng.,' vol. 24, p. 144 (1933).

‖ 'Phil. Mag.,' *loc. cit.*

¶ Schonland and Allibone, 'Nature,' vol. 128, p. 794 (1931).

spark if the conditions of space charge prevailing below a thundercloud are imitated. Such cathode branching in the downward leader, visible in stroke $9c_m$ but too feeble to be recorded in other cases, would satisfactorily explain this curious effect.

Another possibility is that discharges such as $7a_m$, without leaders preceding them, occur after the electricity on the cloud has been removed, in this storm by flashes 5 and 6 at practically the same instant. There remains then the very considerable space charge in the air, first discussed by Wilson,* which will itself cause a discharge to pass from the ground upwards. The discharge though primarily between ground and lower air might, as in $7a_m$, continue onwards to the cloud, with reduced intensity.†

This work is published with the kind permission of the South African Institute of Electrical Engineers, whose financial support has made it possible.

We are specially indebted to Mr. C. J. Monk, M.(S.A.)I.E.E., and Mr. F. C. A. Crewe for their assistance in constructing and testing the camera used, and to Mr. Bernard Price for his assistance and support. We wish also to thank Dr. C. V. Boys, F.R.S., for the loan of his original camera and for much valuable advice and encouragement.

Summary.

(1) Eleven lightning flashes, comprising fifty separate strokes from two separate thunderstorms, have been photographed with a rotating lens camera based upon the design of C. V. Boys. The speed was high enough to permit the study of the propagation of the discharge.

(2) The majority of the strokes were found to be double and to consist of a dart-like downward-moving leader stroke, followed immediately upon arrival at the ground by a more intense flame-like upward-moving main stroke.

(3) The mean velocity found for the leader strokes was $1 \cdot 1 \times 10^9$ cm./sec. along the tortuous track in two dimensions and $7 \cdot 0 \times 10^8$ cm./sec. in the vertical direction. The length of the dart was found to be less than 54 metres.

(4) Corresponding mean velocities for the main strokes were $6 \cdot 0 \times 10^9$ cm./sec. and $3 \cdot 8 \times 10^9$ cm./sec.

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* 'Proc. Phys. Soc.,' vol. 37, p. 32*a* (1925).

† A discussion of the effect of space charge on the lightning flash has recently been given by one of us (Schonland, 'Trans. S. Afr. Inst. Elect. Eng.), *loc. cit.*

(5) The majority of the strokes were unbranched. Four strongly branched tracks have been examined. The branches always developed outwards from the main channel after the discharge had reached the branching point. They travelled with a velocity of the same order as given in (4).

(6) The leader strokes are shown to be identifiable with electron avalanches and the main strokes with thermally ionized channels. The polarity of the discharges was such as to make the cloud-base negative and the earth positive.

The Calculation of Internal Conversion Coefficients of γ-Rays.

By J. B. Fisk, Trinity College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received October 30, 1933.)

The purpose of this paper is the calculation of theoretical values for the internal conversion coefficient, I, of γ-rays converted in the K- and L_I-shells. Hulme* has obtained values for I in the K-shell assuming the radiating nucleus to emit the field of a dipole; while Taylor and Mott† have assumed a quadripole field. The internal conversion coefficient has here been calculated for a number of values of $h\nu$ for the L_I-shell applying the theory developed by Taylor and Mott; the previous results for the K-shell have been extended and slight errors in the region of soft γ-rays have been corrected. Finally, the limiting values for very soft γ-rays have been obtained for both K- and L_I-shells, with both quadripole and dipole fields. The calculations have been carried through using a value of the charge number Z = 84. The correction for RaB (Z = 82) would be small.‡

Recently Taylor and Mott§ have extended their theory to account for the interaction between the nucleus and the extranuclear electrons. They have shown that the "internal conversion coefficients" as calculated in H II and TM I are not a measure of the ratio

$$\frac{\text{Number of } \beta\text{-particles ejected in time } dt}{\text{Number of } \gamma\text{-quanta leaving the nucleus in time } dt},$$

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* 'Proc. Roy. Soc.,' A, vol. 138, p. 643 (1932)—referred to as H II.

† 'Proc. Roy. Soc.,' A, vol. 138, p. 665 (1932)—referred to as TM I.

‡ To the first order, I varies as Z^{-1}; *cf.* H II, equation (29).

§ 'Proc. Roy. Soc.,' A, vol. 141, p. 215 (1933)—referred to as TM II.

but, apart from a factor in general effectively unity, give

$$\mathrm{I} \equiv \frac{\text{Number of } \beta\text{-particles ejected in time } dt}{\text{Number of } \gamma\text{-quanta } \textit{escaping from the system} \text{ in time } dt}.$$

This is the quantity directly measured in the experiments, and, of course, there is a perfectly definite meaning attached to values of this ratio greater than unity, as well as to values less than unity.

Fig. 1 shows the values of I for the K-shell. Curve I is just that which appears in TM I, p. 668, but extended to greater values of θ, *i.e.*, softer γ-rays, and with certain small arithmetical corrections in the region $\theta = 2$. Curve II is the similar calculation of Hulme for the dipole case, while the points marked with a cross show the experimental values.*

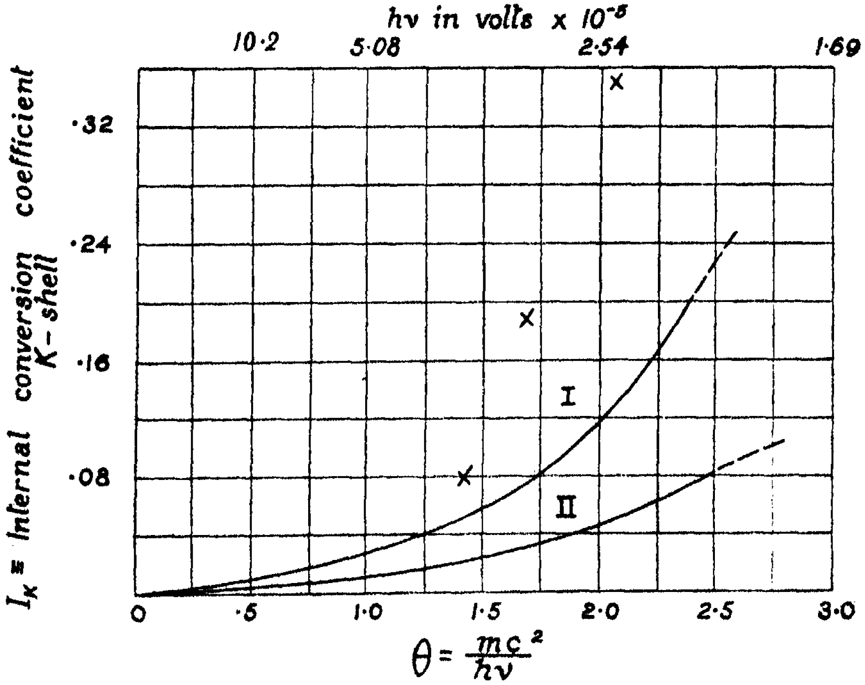

Fig. 1.

Fig. 2 shows the values of I for the $\mathrm{L_I}$-shell. These results were obtained by extending those of TM I in an obvious manner (*cf.* H II, § 5). It is interesting to note here that the B-type solution (*cf.* TM I, equation (2.8)) gives a contribution approximately equal to that arising from the A-type; and later, in the limiting case of very soft γ-rays, that the B-type is predominant, whereas in the K-shell the B-type gives a negligible contribution. This, however, does not represent a physically observable fact, as only the sum of the two types of solutions may be measured.

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* In TM I the calculated values were compared with the experimental values of the quantity α defined in Rutherford, Chadwick, and Ellis, "Radiations from Radioactive Substances," pp. 510 *et seq.* The conclusions of TM II show that the calculated values should be compared with the quantity $\alpha/1 - \alpha$ as tabulated in col. III, p. 512, *ibid.*

Fig. 3 shows the asymptotic behaviour of I for very soft γ-rays. Curves I and II are for the K-shell, quadripole and dipole respectively; while curves L_Q and L_D are the corresponding values of I for the L_I-shell. The exact shape of the curve between values of $\theta = 3\cdot5$ and $\theta = 18\cdot5$ is unknown, for in this region the hypergeometric series used in the calculations converge very slowly, and it is impracticable to evaluate them. We see here that I is much greater for soft γ-rays in the limit in the L_I-shell than in the K-shell; also, that the quadripole values are always greater than the corresponding dipole values. For γ-rays of $h\nu \doteqdot 0\cdot275 \times 10^5$ electron-volts (*i.e.*, the softest γ-rays which could be converted in the L_I-shell) the theory predicts almost complete conversion in the L_I-shell. The only body for which experimental values have been obtained for very soft γ-rays is RaD, and even here there must be con-

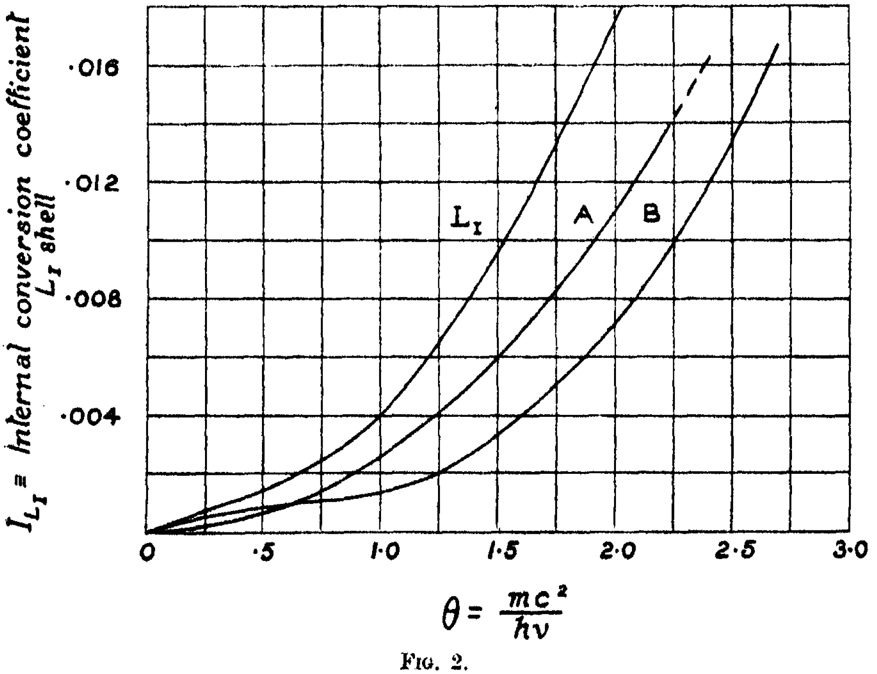

FIG. 2.

siderable doubt about the exact figure. Gray and O'Leary* obtained the value marked with a cross at about $\theta = 10 \cdot 7$, and it will be seen that this lies close to the dipole curve. It is possible, however, that the value may be higher, and it will be noted that if this were so agreement might still be possible with the quadripole curve. In view of the uncertainty of the data, this comparison cannot be pushed further at present.

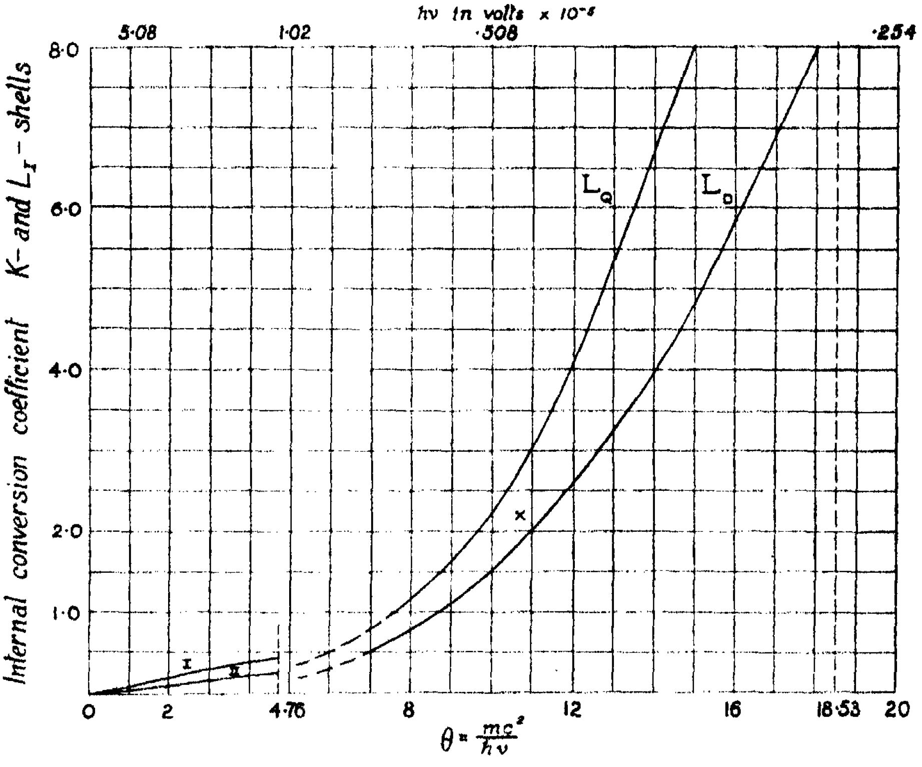

FIG. 3.

The asymptotic values were obtained by letting q/a tend to infinity, *i.e.*, by letting the energy of the outcoming ray approach a value just sufficient to eject an electron from each particular shell. The numerical work was done using the relationships of type H II, p. 652 (18), instead of (20), for, in the present instance, the z of the hypergeometric series is very small.

Asymptotically for hard γ-rays, *i.e.*, when $q/a \rightarrow 0$, the internal conversion is the same for quadripole radiation as for dipole radiation. The ratio of I in the K- and L_I-shells for quadripole reduces to just that obtained for dipole, namely,

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* 'Nature,' vol. 123, p. 568 (1929).

$$\frac{I_{L_I}\text{ asymptotic}}{I_K\text{ asymptotic}} = \frac{(N+2)\,.\,e^{-2\,.\,\gamma\,\text{arc tan}\,(\gamma/(\beta+2))}}{2\,.\,(N-1)\,N^{(2\beta+4)}}.$$

This ratio is about 1 : 6·7, which is in agreement with experiment for this region. The ratio 1 : 6·7 remains practically constant for calculated values of I_{L_I}/I_K up to $\theta = 2$.

I should like to take this opportunity to thank Dr. Hulme for permission to use some of his dipole results; and Dr. C. D. Ellis for discussion on the subject. I am deeply indebted to Mr. H. M. Taylor for help and encouragement throughout this work.

Summary.

The internal conversion coefficient of γ-rays has been calculated for the L_I-shell of RaC, assuming the nucleus to radiate the field of a quadripole. The previous K-shell results have been extended, and slight errors in the region of soft γ-rays have been corrected. Limiting values for very soft γ-rays for the K- and L_I-shells, quadripole and dipole, have been obtained.

The ratio of internal conversion in the K- and L_I-shells is about 1 : 6·7 for hard γ-rays, and remains nearly constant up to a value of θ ($= mc^2/h\nu$) of 2. The theory predicts very nearly complete conversion in the L_I-shell for the softest γ-rays which could be converted in that shell.

A New Method of Calculating the Mean Value of $1/r^s$ for Keplerian Systems in Quantum Mechanics.

By J. H. VAN VLECK, University of Wisconsin.

(Communicated by P. A. M. Dirac, F.R.S.—Received November 3, 1933.)

The usual method of calculating the diagonal matrix elements of an integral power of the radius r in an inverse square quantum system is that due to Waller.* His procedure is based on the Schrödinger form of the theory, and utilizes in particular the generating series for the Laguerre polynomials. For negative powers, Dirac's very elegant theory of "q-numbers,"† developed in these 'Proceedings' during the early days of quantum mechanics, furnishes an interesting alternative method which appears to have been overlooked, and which we believe is easier. From his theory the following rule can be derived:

Suppose that we desire the mean value (diagonal element) of $1/r^s$, where s is an integer greater than unity. We write down the expression

$$\mathrm{A}\,(\alpha_l + \beta_l\, e^{-i\chi} + \gamma_l\, e^{i\chi})^{s-2} \tag{1}$$

with

$$\mathrm{A} = \frac{16\pi^4 m^2 Z^2 e^4}{(l+\frac{1}{2})\, n^3 h^4}, \quad \alpha_l = \frac{4\pi^2 m Z e^2}{h^2 l\,(l+1)}, \quad \beta_l = \frac{2\pi^2 m Z e^2}{h^2\,(l+\frac{1}{2})\,(l+1)}\left[1 - \frac{(l+1)^2}{n^2}\right]^{\frac{1}{2}},$$

$$\gamma_l = \frac{2\pi^2 m Z e^2}{h^2 l\,(l+\frac{1}{2})}\left[1 - \frac{l^2}{n^2}\right]^{\frac{1}{2}}. \tag{2}$$

Because of the q-nature of the algebra, the symbols α_l, β_l, γ_l are not to be construed as commuting in multiplication with the exponentials, and instead obey the relations

$$e^{i\chi} f_l = f_{l-1}\, e^{i\chi}, \quad e^{-i\chi} f_l = f_{l+1}\, e^{-i\chi} \quad (f_l = \alpha_l,\ \beta_l, \text{ or } \gamma_l). \tag{3}$$

By means of (3) one can reduce (1) to a terminating Fourier series

$$\sum_m b_m\, e^{im\chi}, \tag{4}$$

wherein the important feature is that the coefficients appear only in front of the exponentials. *The constant term b_0 in (4) is then the desired mean value.* We omit the proof, but it can readily be supplied from the theory in section 7 of Dirac's paper. This result may be regarded as the quantum analogue of the well-known classical relation

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* 'Z. Physik,' vol. 38, p. 635 (1926).

† 'Proc. Roy. Soc.,' A, vol. 110, p. 561 (1926).

$$\overline{\frac{1}{r^s}} = \frac{1}{2\pi a^2 (1-\varepsilon^2)^{\frac{1}{2}}} \int_0^{2\pi} \left[\frac{1+\varepsilon\cos\phi}{a(1-\varepsilon^2)}\right]^{s-2} d\phi,$$

in which a and ε denote respectively the semi-major axis and eccentricity.

From the above rule one sees, almost by inspection, that the mean values of r^{-2}, r^{-3} and r^{-4} are respectively A, $\mathrm{A}\alpha_l$, and $\mathrm{A}(\alpha_l^2 + \beta_l\gamma_{l+1} + \beta_{l-1}\gamma_l)$. On substituting the explicit values in terms of the principal quantum number n and azimuthal quantum number l, by means of (2), one finds that these are the same formulæ as those given in the literature.[*] The expressions for the mean values of $1/r^5$ and $1/r^6$ are more complicated and do not appear to have previously been published. They are, however, sometimes useful,[†] and are as follows :—

$$\overline{\frac{1}{r^5}} = \mathrm{A}\,\{\alpha_l(\alpha_l^2 + \beta_l\gamma_{l+1} + \beta_{l-1}\gamma_l) + (\alpha_l + \alpha_{l-1})\,\beta_{l-1}\gamma_l + (\alpha_l + \alpha_{l+1})\,\beta_l\gamma_{l+1}\},$$

$$\overline{\frac{1}{r^6}} = \mathrm{A}\,\{(\alpha_l^2 + \beta_l\gamma_{l+1} + \beta_{l-1}\gamma_l)^2 + \beta_l\beta_{l+1}\gamma_{l+1}\gamma_{l+2} + (\beta_{l-2}\beta_{l-1}\gamma_{l-1}\gamma_l) + (\alpha_l + \alpha_{l+1})^2\,\beta_l\gamma_{l+1} + (\alpha_l + \alpha_{l-1})^2\,\beta_{l-1}\gamma_l\}.$$

Explicit formulæ in terms of n, l are immediately obtainable by substitution from (2). As they are not especially compact, it is more convenient to give instead the numerical forms appropriate to d, f, and g states :—

	$\overline{\frac{1}{r^5}} \times \frac{a_0^5}{Z^5}$
$l = 2$ (d states)	$0{\cdot}007937n^{-3} - 0{\cdot}02698n^{-5}$
$l = 3$ (f states)	$0{\cdot}0005292n^{-3} - 0{\cdot}003704n^{-5}$
$l = 4$ (g states)	$0{\cdot}00008016n^{-3} - 0{\cdot}0009461n^{-5}$

	$\overline{\frac{1}{r^6}} \times \frac{a_0^6}{Z^6}$
$l = 2$ (d states)	$0{\cdot}06173n^{-3} - 0{\cdot}27336n^{-5} + 0{\cdot}12698n^{-7}$
$l = 3$ (f states)	$0{\cdot}00011223n^{-3} - 0{\cdot}0010742n^{-5} + 0{\cdot}0011543n^{-7}$
$l = 4$ (g states)	$0{\cdot}000008633n^{-3} - 0{\cdot}00014183n^{-5} + 0{\cdot}0002664n^{-7}$

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[*] *Cf.*, for instance, Pauling and Goudsmit, "The Structure of Line Spectra," p. 32.

[†] This mean value of $1/r^6$ is needed for the quadrupole corrections in calculations on atomic spectral terms, and was used in Whitelaw and the writer's article on the aluminium spectrum ('Phys. Rev.,' vol. 44, p. 551 (1933)). I am indebted to Dr. Whitelaw for calculation of the numerical form in the case $s = 6$.

Here a_0 is the usual Bohr radius unit $a_0 = h^2/4\pi^2 e^2 m$. The corresponding values for s and p states are infinite, as could also have been predicted from the behaviour of the wave functions at the origin.

By means of the rule based on (1), one can easily see that with any integral $s > 1$, the mode of dependence on n is, just as in classical theory, of the form

$$\frac{1}{r^s} = \frac{1}{n^3}\left(C_0 + \frac{C_2}{n^2} + \frac{C_4}{n^4} + \dots + \frac{C_k}{n^k}\right), \tag{5}$$

where k equals $s - 2$ or $s - 3$ according as s is even or odd. The coefficients in (5) are, however, different functions of l in quantum and classical mechanics.

Phenomena Associated with the Anomalous Absorption of High Energy Gamma Radiation.—II.

By L. H. Gray, Ph.D., Fellow of Trinity College, Cambridge, and G. T. P. Tarrant, Ph.D., Pembroke College, Cambridge.

(Communicated by Lord Rutherford, O.M., F.R.S.—Received November 7, 1933.)

§ 1. *Introduction.*

In a previous paper* we gave an account of an investigation of the secondary radiation produced when different elements are irradiated with the high energy γ-rays of thorium C″. The present paper describes an extension of this investigation.

It will be recalled that confusion with the ordinary scattered radiation was almost entirely eliminated by examining the secondary radiation in a direction making a large angle with the primary beam, since under these conditions not only is the Compton radiation relatively very much weaker, but in addition it is comparatively soft and is easily absorbed in the radiator itself, or in a very small thickness of absorber, owing to the large increase in wave-length at this large angle of scattering.

In addition to a weak Compton scattered radiation, a secondary radiation was observed which was more strongly absorbed in lead than the primary radiation. While our experiments were in progress similar observations were reported by Chao,[*] who estimated the wave-length of this secondary radiation at 20 X.U. ($0 \cdot 6 \,.\, 10^6$ e-volts). He found also that the radiation was emitted in about the same intensity in a number of directions making angles of between 30° and 150° with the primary beam. Assuming that the intensity was independent of the angle of emission, or that it was varying in accordance with the Thomson formula, we were able to show from our measurements at 125° that the secondary emission was of the same order of magnitude as the observed anomalous absorption, and that this was true for all the elements investigated. We showed also, by two independent methods, that the observed secondary radiation was derived very largely from the interaction of quanta of energy at least as great as $2 \cdot 0 \,.\, 10^6$ volts, in agreement with Chao's observation by an absorption method.[†]

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* 'Proc. Roy. Soc.,' A, vol. 136, p. 662 (1932). This will be referred to subsequently as Part I.

Meitner and Hupfeld,[‡] who irradiated lead with hard radium C γ-rays, could observe only the hard component of the radiation since the soft component observed by Chao and ourselves, and reported on recently by Stahel and Ketelaar,[§] would be difficult to disentangle from the Compton scattered radiation at their angle of observation (90°). Meitner and Hupfeld believe that the absorption coefficient of the hard component which they observed was somewhat greater than the value we published, but there is certainly no experimental ground for doubting the existence of the softer radiation which we believe contains two-thirds of the energy of the secondary emission from lead, and almost the entire emission from light elements.

It seems clear, therefore, that radiation having a quantum energy of the order of two million volts is capable of a new type of atomic interaction, in which a considerable part of the energy is transformed into a radiation having the appearance of a γ-radiation of half a million volts quantum energy.

No adequate theoretical account of the nature of the interaction has so far been given. Indeed it seems likely that we have to do with a type of interaction essentially different from those manifested by the extranuclear electronic system. For this reason, our first concern has been to ascertain as accurately as is possible by absorption methods the nature of the secondary radiation emitted by different elements when excited by the γ-rays from both radiothorium and radon sources.

[*] 'Phys. Rev.,' vol. 36, p. 1519 (1930).

[†] 'Proc. Roy. Soc.,' A, vol. 136, p. 206 (1932).

[‡] 'Z. Physik,' vol. 75, p. 705 (1932).

[§] 'C. R. Acad. Sci. Paris,' vol. 196, p. 1664 (1933).

We do not wish to prejudice the issue by referring to the phenomenon as "nuclear" absorption. The fact that, for the very limited wave-length range in which the phenomenon is at present known, the probability that the quantum will undergo transformation in a given thickness of material is roughly equal to the target area presented by the nuclei of the atoms concerned does seem to supply some justification for the title employed, but this numerical agreement may be misleading. The term "secondary nuclear radiation," which has been used previously, is still employed for convenience, but without implying that the radiation can be related to any known nuclear process.

§ 2. *Modifications in the Experimental Arrangement.*

The arrangement of source, radiator, and ionization chamber was exactly as in our former experiments (see fig. 1, *loc. cit.*, p. 665). The arrangement was, however, improved in the following respects. The apparatus was transferred to a much larger room and the ionization chamber was set up on top of a tall brick column so as to diminish the effect of secondary radiation from the walls of the room and from the floor. Separate radiators of each element investigated were constructed of nearly identical geometrical form, and could be placed in position, or removed, rapidly by means of an overhead railway. The beginning and end of each ionization current measurement were observed visually, but during measurements of long duration (5–15 minutes) the potentiometer arm (which changed the potential of one plate of the condenser used in the Townsend balance method) was moved as required by a motor controlled by a photoelectric cell, valve, and relay.

The measuring apparatus, electrometer, etc., were removed to a distance of 6 metres from the ionization chamber and every part of the guard tube system was evacuated (by a Hyvac pump) right up to the quartz insulators on the ionization chamber. The Compton electrometer, earthing key, and balancing condenser were mounted inside a bell-jar and evacuated to 1 cm. Hg pressure.

As a result of these improvements it was possible to obtain high accuracy in the measurements even when an unscreened source of 250 mg. activity was in position beneath the lead cone. The probable statistical errors of individual measurements of the smallest ionization currents was 0·5 J, which was always less than 2% of that part of the ionization due to the radiation under investigation. Moreover, since a single measurement took only 10–15 minutes, it was practicable to obtain, if desired, higher accuracy by increasing the number of observations.

§ 3. *The Reliability of the Experimental Data and their Interpretation.*

This may conveniently be considered in three sections :—

(*a*) The inclusion in the observed ionization of contributions from sources other than the secondary nuclear radiation from the radiator.

(*b*) The accuracy with which the absorption curve of the nuclear radiation can be corrected to standard conditions, *i.e.*, to conditions such that the absorption coefficient derived directly from the curve is equal to the sum of the coefficients σ_a, σ_s, τ, etc.

(*c*) The extent to which the inaccuracy of the individual measurements may introduce uncertainty into the analysis of the absorption curve.

(*a*) *The Ionization due to Extraneous Sources.*—By considering only the difference between the ionization observed with and without the radiator in position (source present) allowance is automatically made for all sources of extraneous ionization except any natural activity of the radiator, the absorption by the radiator of natural or secondary γ-radiation from the walls of the room, and Compton scattered radiation from the radiator.

If the specific natural activity of the material of the walls and of the radiators (expressed as γ-ray emission per electron) were the same, the absorption in the radiator of the radiation from the walls would have been balanced by the activity of the radiators, exactly for light elements, and approximately for the lead radiator. The lack of balance was investigated experimentally for each radiator used, with five different thicknesses of absorber round the chamber. The walls were always considerably more active than the radiator, but the correction was in general extremely small, never exceeding 5% of the ionization due to the nuclear radiation. Lead, tin, copper, iron, and coal appeared all to have about equal activity, while coal ash was considerably more active, suggesting that the radioactive material was left behind during combustion, and was probably therefore associated with the mineral constituents, even in the coal itself.

With the new experimental arrangement, the ionization chamber was at a vertical distance of about 2 metres from the floor and roof, and at a mean distance of 5 m. from the walls, as compared with 2 m. previously. In this way the correction for the absorption by the radiator of secondary radiation from the walls was greatly reduced. It now amounts to only 2% of the nuclear radiation from the lead radiator. Though bigger relatively for the lighter elements it has a negligible influence on the shape of the absorption curves, since it is found that the nuclear part of the radiation is indistinguishable in quality from the nuclear radiation from these elements, and the experimental investigation of the Compton scattered radiation discussed below includes the correction for any radiation Compton scattered by the walls of the room.

This apparent identity of the nuclear radiation emitted at 175° by the walls with that emitted by the lighter elements at 125° is easily seen by comparing the curves of figs. 5 and 7 with those of fig. 1. in which the nuclear radiation is easily distinguished from the very soft Compton radiation, which has an absorption coefficient in lead of 13 cm.$^{-1}$.

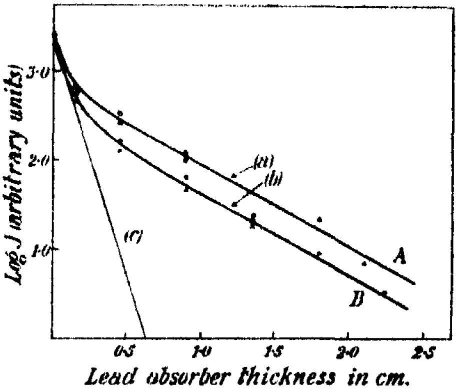

FIG. 1.—Logarithmic absorption curves of secondary emission at 175° (from the walls of the room).

(*a*) △ ○ radiothorium source ; $\mu = 2\cdot0$ cm.$^{-1}$ } scaled to the same strength.
(*b*) ● × radon source, nuclear radiation }

Relative intensity of secondary emission is approximately the same as at 125°.
(*c*) $\mu = 13$ *cm.*$^{-1}$, *Compton radiation.*

Compton Scattering from Carbon determined Experimentally.—After applying the relatively unimportant corrections just referred to, the absorption curves differ from those of the pure nuclear radiation only through the presence of Compton scattered radiation which, on account of its very much longer wavelength and absorbability, affects only the first centimetre of the absorption curve. In our former measurements its magnitude at each point of the absorption curve was calculated, using the Klein-Nishina formula.

Since we are now specially interested in any possible admixture of softer nuclear radiation, the magnitude of the Compton scattering has been determined experimentally by constructing a container of wood and "beaverboarding" of exactly the same inside diameter and height as the other radiators, and filling this with such a weight of coal as to obtain the same mass per unit area. From fig. 2 it will be seen that only a small proportion of the secondary radiation from coal is of nuclear hardness. It was thus possible to obtain an accurate estimate of the Compton scattering for both radiothorium and radon sources. The Compton scattering from other radiators of low atomic number will, of course, be the same as from coal. For lead, and to a small extent, tin, it was necessary to make allowance for photoelectric reabsorption in the radiator, but since (*cf.* fig. 2, *b*) the experimentally observed values for coal were in good agreement with our former calculated estimate, the correction was easily made.*

(*b*) *Correction of Absorption Curves to "Standard Conditions."*—It is now generally recognized that the estimation of the quantum energy of γ-radiation by absorption methods, in which the absorber is placed close to the ionization chamber, is subject to error on account of the scattered radiation which enters the chamber. While this error may be serious for very hard radiation, its

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* *Note added in Proof, January* 2, 1934.—Radiation deflected through a given angle by two scattering processes may suffer a smaller change in wave-length than that corresponding to a single deflection through the same angle, and it has been suggested that such "double scattered" radiation may be making an appreciable contribution to what we have regarded as "nuclear radiation." The ThC″ hard line, twice scattered, and emerging at 125°, would consist of a broad band having an effective wave-length of about 35 X.U. ($\mu_{Pb} = 3 \cdot 0$ cm.$^{-1}$) which would not be easily confused with nuclear radiation ($\mu_{Pb} \sim 2 \cdot 0$ cm.$^{-1}$) unless present in relatively small intensity. An upper limit to this intensity may be derived from the consideration that the absolute magnitude of double scattering will be greatest for light elements, and, for sources of equal strength, would be expected to be somewhat greater in the case of the RaC γ-rays. At any given absorber thickness it will, therefore, not be greater than the carbon-radon value. The following figures give the nuclear ionization per milligram activity at 0·90 cm. lead absorber (see Table II). Analogous figures would be obtained at other absorber thicknesses.

	Lead.	Tin.	Iron.	Carbon.
ThC″ γ-rays	21·1	13·9	8·0	2·1
Radon source	7·8	4·8	3·3	0·6

It follows immediately that double scattering cannot account for more than 0·6 J at this absorber thickness. Since this shows a genuine nuclear effect of at least 1·4 J from carbon excited by ThC″ γ-rays, it is certain that some part of the 0·6 J excited by RaC γ-rays must also be nuclear radiation. Thus it is improbable that as much as 0·3 J is the actual contribution from double scattering, which must be compared with values ranging from 3 J to 20 J for the nuclear radiations. It seems clear, therefore, that double scattering cannot influence appreciably either the comparison of the radiation excited by RaC and ThC″ γ-rays (p. 702) or the absolute intensity of the emission from heavy elements (Part III, § 3).

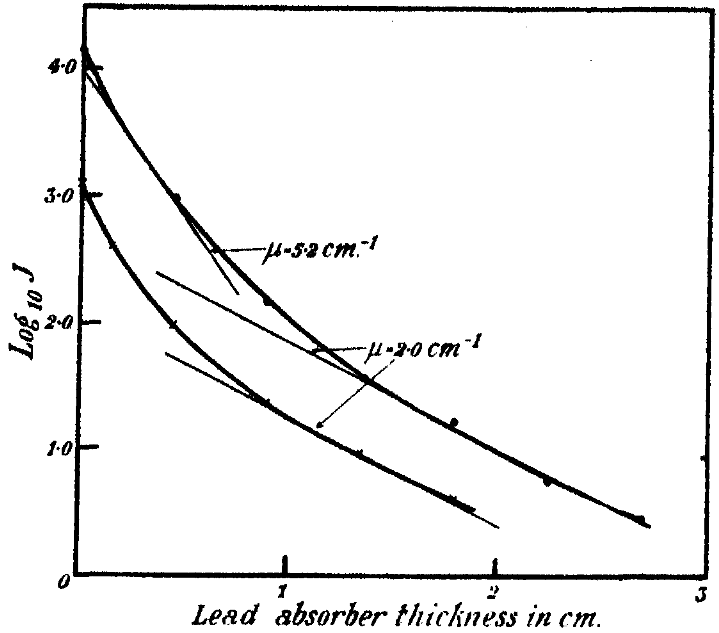

FIG. 2.—(*a*) Secondary radiation from a carbon radiator; • radon source, × radiothorium source.

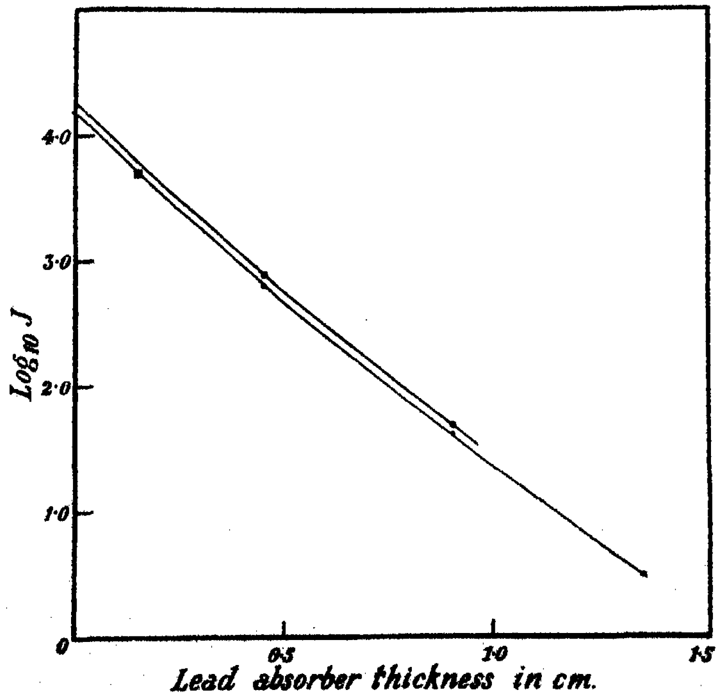

FIG. 2.—(*b*) Absorption of thorium C″ γ-rays Compton scattered through 125° by carbon radiator; • Calculation; □ Experiment.

importance is often greatly over-estimated for softer radiations. Clearly the correction cannot be a large one, if lead absorbers are employed, for an absorption coefficient under standard conditions may be denoted as $(\sigma_a + \sigma_s + \tau)$ and—even if the whole of the scattered radiation were to enter the chamber—it cannot be smaller than $(\sigma_a + \tau)$.

With our experimental arrangement the actual correction is obviously smaller than this upper limit by a factor of about three, since (*a*) the solid angle subtended by the chamber at the absorber is always much less than 4π, and is reduced to a half for all radiation hitting the top, bottom, or edges of the absorber; (*b*) the scattered radiation has a much lower quantum energy than the primary, and so will be very heavily absorbed in penetrating the chamber wall and the thickness of lead absorber which is already in position.

This scattering correction (which is greatest for hard radiation) has been calculated for $2 \cdot 6 \,.\, 10^6$ volt radiation, and the calculated absorption coefficients have been confirmed by experiment to within 5%.* The same calculation shows that the correction is small in the region of half a million volts, and it is worth noting that if it has been underestimated it will make the radiation appear harder, and not softer, than it really is.

Since a *cylindrical* ionization chamber is used in our experiments, so that the absorbers consist of cylindrical sheets, the primary radiation will in general traverse more than the *radial* thickness of the absorber, and the apparent absorption coefficient will be thereby increased. Over the range of quantum energy $0 \cdot 5$–$1 \cdot 0 \,.\, 10^6$ volts (which includes the secondary nuclear radiation) these two errors almost exactly cancel, so that for radiation of this hardness a cylindrical ionization chamber may be used without correction in estimating the quantum energy of the γ-ray beam to an accuracy of a few per cent.

From the point of view of γ-ray technique this result is most important since it is almost always more convenient to place the absorber close to (or completely surrounding) the ionization chamber, and in the investigation of weak radiation this is usually the only possible arrangement.

In our previous paper we may have given an entirely erroneous idea of the magnitude of this correction by tabulating the integrated change in ionization due to the change in absorption coefficient over the whole absorber thickness, so that it appeared very important at the larger absorber thicknesses, where the correction to the *absorption coefficient* is in reality quite small, as will be seen from the figure.

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* A full account of the method of calculation and the experimental confirmation has been published elsewhere. Tarrant, 'Proc. Camb. Phil. Soc.,' vol. 28, p. 475 (1932).

Although there was no reason to suspect the calculations it seemed desirable to check them experimentally. Clearly the object of such a test must be to find to what extent an absorption coefficient measured under the usual experimental conditions differed from the true value obtained with a parallel γ-ray beam and a plane absorber so arranged that no scattered radiation enters the ionization chamber. In practice, this is a matter of considerable difficulty, so that without great care the experimental results may be very misleading. Since the magnitude of the correction varies with wave-length, a primary beam of about the right hardness was obtained by scattering ThC″ γ-rays through about 90°. This beam was naturally somewhat inhomogeneous, but, having predominant wave-lengths intermediate between the two components of the nuclear radiation it was satisfactory for the purpose in hand. This "source," comprising a hollow cylindrical block of iron with a small source situated on the axis and a lead cone to absorb the rays going directly to the chamber, is shown to scale in fig. 4, *a* and *b*.

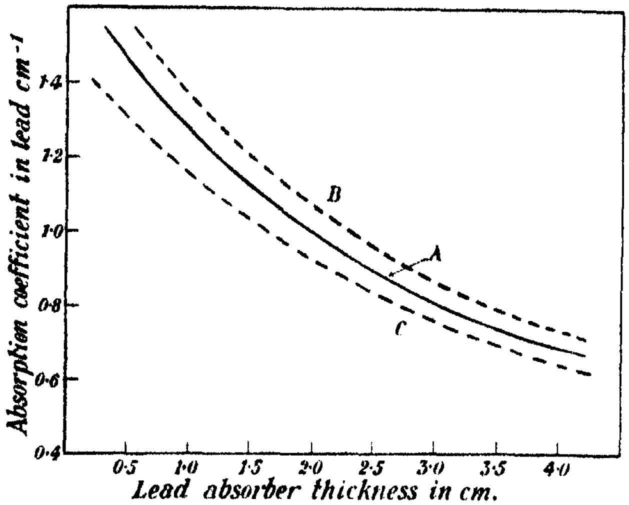

FIG. 3.—A, fully corrected absorption coefficient, coinciding approximately with uncorrected curve. B–A, correction for increased path of non-radial rays. C–A, correction for scattering into the ionization chamber.

The composite source was 200 cm. from the ionization chamber. Circular lead discs of diameter just sufficient to absorb all the rays going though the chamber, and of total thickness 0·75 or 1·5 cm. were suspended by wires 36 cm. in front of the source.

Absorption coefficients measured with this disposition of apparatus were compared with values obtained when the same thickness of absorber was placed round the ionization chamber as in the main series of measurements, with results shown in Table I.

Table I.

		Total absorber.	Thickness.
		1·35–2·10 cm.	1·35–2·85 cm.
Calculated corrections	Scattering	−6·5%	−6·0%
	Increased path	+3·2%	+3·0%
	Resultant correction	−3·3%	−3·0%
Experiment	Absorber in standard position	$\mu = 1{\cdot}21_0$ cm.$^{-1}$	$\mu = 1{\cdot}16_0$ cm.$^{-1}$
	Experimental conditions, absorber round chamber	$\mu = 1{\cdot}12_7$ cm.$^{-1}$	$\mu = 1{\cdot}07_1$ cm.$^{-1}$
	Difference	$\Delta\mu = -0{\cdot}08 \pm 0{\cdot}02$	$\Delta\mu = -0{\cdot}09 \pm 0{\cdot}02$
	% correction	−6·7 ± 2%	− 7·2 ± 1·5%

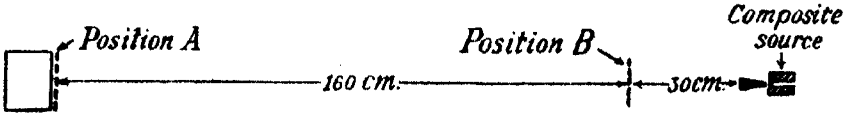

FIG. 4.—(*a*) Scale diagram. Position A, absorber round chamber, "experimental conditions"; position B, "standard conditions."

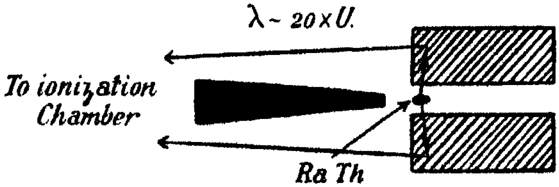

FIG. 4.—(*b*) The "composite source."

The calculated final correction is thus seen to be some 4% smaller than was observed experimentally. The discrepancy may be due to experimental inaccuracy in excess of the probable error (1·5%); it might, on the other hand, be caused by excessive scattering by the lead, not hitherto suspected in this region of wave-length. This possibility has not been thoroughly investigated.

These experiments thus lead to 5% as a probable upper limit to *systematic* errors in the absolute value of absorption coefficients derived from the corrected absorption curve discussed in the following sections. The corresponding error in the quantum energy of the radiation is only 2·5%, so that the experimental accuracy considerably exceeds the reliability of the $\mu - \lambda$ curve by means of which absorption coefficients are translated into quantum energy.

(*c*) *The Analysis of the Absorption Curves.*—When the radiation under examination is predominantly of one wave-length, this figure (5%) may be taken as the accuracy with which the absorption coefficient of the radiation is known. When it is inhomogeneous, however, there is a new source of uncertainty, viz., in the *analysis* of the curve into linear components. Unless each individual experimental point on the absorption curve is known with an accuracy far exceeding 1% an analysis which attempts to reveal more than two or three predominant components (strong lines or relatively narrow bands) is meaningless. In what follows we shall only be concerned with the broad analysis into predominant components. Such an analysis is usually made by trial and error, operating on a *smoothed* absorption curve, and experience shows that the limits of error assigned to the resulting absorption coefficients is very largely controlled by psychological inclinations. To eliminate this source of dispute we examined one of our curves in greater detail. It comprises two well-marked components, having $\mu_1 = 0\cdot75$ cm.$^{-1}$ and $\mu_2 = 1\cdot95$ cm.$^{-1}$, the initial ionization due to the two components being in the ratio $K = 0\cdot554$. Treating μ_1, μ_2, and K as variables, it was possible to write down five inequalities involving $\delta\mu_1$, $\delta\mu_2$, and δK, representing the fact that the curve must be within the limit of experimental error at five equally spaced experimental points covering a total thickness of 3 cm. of absorber (lead). The actual values assigned to the errors were 3% at the last point and 2% at the others—values considerably in excess of our *probable* errors. The following changes in the constants were found to be just not allowable :—

$$\Delta\mu_1 = \pm 15\% \qquad \Delta\mu_2 = \pm 25\%$$

or

$$0\cdot65 < \mu_1 < 0\cdot85 \text{ cm.}^{-1} \qquad 1\cdot41 < \mu_2 < 2\cdot45 \text{ cm.}^{-1}.$$

These limits are surprisingly wide, and show that in *any* absorption measurement very high experimental accuracy is necessary to secure a reasonable certainty in the analysis even in a favourable case such as we have chosen, in which the components are well separated in absorption coefficient and of comparable intensity.

(*d*) *The Relation between Absorption Coefficients and Wave-length.*—It is assumed that, for quantum energies less than $2 . 10^6$ volts (*i.e.*, outside the region of nuclear interaction) the absorption coefficient μ is equal to $\sigma + \tau$, where σ is given by the Klein-Nishina formula and τ in lead is given by the empirical formula

$$\log_{10} \tau = \bar{3}\cdot6505 + 1\cdot0 \log_{10} \lambda + 0\cdot480 (\log_{10} \lambda)^2.$$

These values would appear to be too small as judged by the approximate calculations of Sauter. A calculation has recently been made, however, by a rigid though laborious method by Hulme and McDougall.[†] At the one value of the quantum energy ($1 \cdot 1 \, . \, 10^6$ volt) for which the calculations have been completed, there is good agreement with the empirical formula given above.[‡]

We feel that the empirical formula is to be preferred, until the accurate calculations have been completed, since it is based on the experimental evidence presented elsewhere,[§] and accounts accurately for the absorption of the Compton scattered radiation observed in our experiment at 125°, *i.e.*, is approximately correct at $0 \cdot 3 \, . \, 10^6$ ε-volts as well as at $1 \cdot 1 \, . \, 10^6$ ε-volts as indicated by the above-mentioned calculations.

We believe that it may be considered accurate to 10% everywhere in this region.

§ 4. *The Absorption Curves of the Secondary Radiations.*

The experimental absorption curves (fully corrected) for the secondary radiations excited by the γ-rays from radiothorium and radon sources are shown in figs. 5 and 7 and in Table II.

Table II.

Radiothorium Source. 17·0 mg. S = 650.

Lead absorber thickness, cm. :	0.	0·15	0·45	0·90	1·35	1·80	2·10	2·25	2·85	3·15	3·6	4·35
Lead radiator	1190	1043	690	359	200	—	84·5	—	44·3	—	24·2	—
Tin	1240	966	506	236	113	—	41·5	—	—	—	—	—
Copper	630	565	327	137	60·1	—	18·2	—	—	4·0	—	—
Iron	823	643	321	140	62·2	—	18·0	—	—	—	—	—
Potassium (K_2SO_4)	263	—	141	71	21	—	6·3	—	—	—	—	—
Carbon* (coal)	209	158	91	35·4	16·8	7·9	—	2·5	—	—	—	—

Radon Source.

All values are scaled to initial activity of 210 mg. and S = 650.

Lead	5602	5469	3273	1645	814	—	316	—	151	—	78·1	46·7
Tin	9600	5240	2611	1020	423	—	144	—	61·0	—	33·6	20·5
Iron	8300	3282	1733	697	243	—	69·3	—	37·2	—	—	—
Carbon*	552	433	261	119	57	—	—	—	—	—	—	—

* Only these values are corrected for wall scattered radiation.

[†] 'Nature,' vol. 132, p. 352 (1933).

[‡] The empirical curve is also in very good agreement with (unpublished) measurements made by Dr. C. Lauritsen at Pasadena, using a monochromatic 600 kV. X-ray beam.

[§] L. H. Gray, 'Proc. Camb. Phil. Soc.,' vol. 27, p. 103 (1931).

Carbon—Excited by ThC'' and RaC γ*-rays.*—The absorption curves for the total secondary radiation, fig. 2, are easily resolved into a soft component—Compton scattered radiation—and a harder radiation represented by the approximately linear portion of the curves between 1·35 and 3·15 cm. of lead absorber. The absorption curve of the Compton scattered radiation alone obtained in this way is compared with the calculated Compton scattering in fig. 2*a*, where it will be seen that the agreement is very satisfactory.

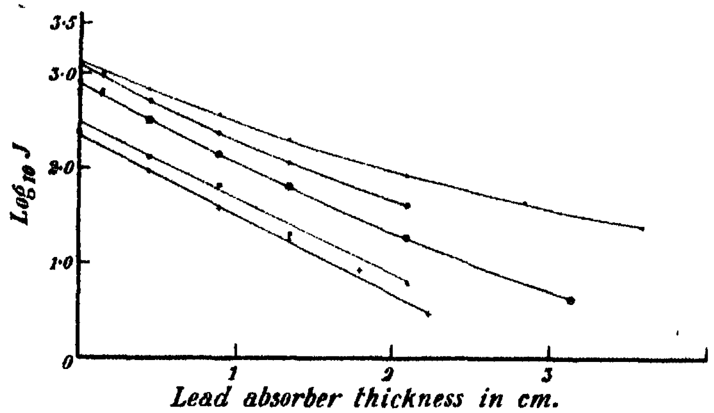

Fig. 5.—Emission at 125° excited by thorium C'' γ-rays. ●, lead ; ⊗, tin ; ×, iron ; ○, copper ; □, potassium sulphate ; +, coal.

The harder radiation is almost entirely "nuclear" radiation, since it has approximately the same absorption coefficient as the nuclear radiation from other light elements, figs. 5 and 7, and falls into line with these also as regards intensity. To make quite sure that it was not due to the mineral constituents of the coal, the experiment was repeated with "ash." The nuclear component of the secondary radiation from the ash was only about one and a half times as intense as that from coal, and since the proportion of ash was only about 7% there appears no doubt that the nuclear radiation was due to interaction with carbon. It will be recalled that in our previous measurements we obtained evidence of nuclear radiation also from oxygen (water). It seems of special theoretical interest that two elements having atomic weights of the simple 4*n* type and which are not generally considered to contain free neutrons should show similar behaviour to elements of more complex constitution.

Iron, Tin, and Lead—Excited by ThC'' γ*-rays.*—The values given in Table II and fig. 5 are all fully corrected (after subtracting Compton radiation) and represent the ionization per unit volume produced in a chamber containing nitrogen at 87 atmospheres (15° C.) the primary source having for each value

17·0 mg. activity. They do not, however, represent exactly the magnitude of the secondary emission per electron, because the geometry, density, and reabsorption are all slightly different for the different radiators. They are in good agreement with our previous results,[*] and show clearly the gradual increase in the proportion of hard radiation with increasing atomic number.

Copper—Excited by ThC″ γ-rays.—This is the first element of odd atomic number to be investigated, and is of special interest in connection with the interaction mechanism suggested by Gamow,[†] according to which the absorption of γ-radiation by such a nucleus should give rise, in addition to other radiation, to the emission of one quantum of a very penetrating radiation, corresponding to the formation of an α-particle from 2 protons and 2 neutrons. From our experiments it is certain that no penetrating radiation is emitted with as much as 1% of the theoretical intensity. Both as regards quality and intensity the radiation is in excellent agreement with the uniform progression noted above. The absorption curve is, in fact, indistinguishable from that of iron.

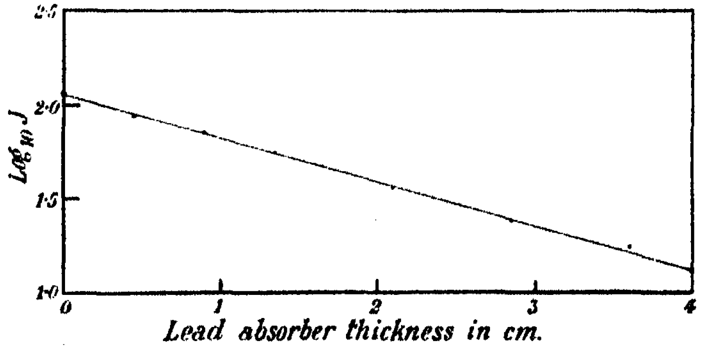

Fig. 6.—Natural γ-radiation of potassium.

Potassium—Excited by ThC″ γ-rays.—In view of the natural radioactivity of potassium it seemed worth while to look for any abnormality in the secondary γ-ray emission. The potassium was used in the form of 3 cwts. of K_2SO_4 contained in the same cardboard container used to examine coal.

It was, of course, necessary to examine first the absorption curve of the natural γ-radiation, fig. 6, which is seen to be approximately linear, representing a homogeneous radiation of quantum energy $2 \cdot 0 \, . \, 10^6$ ε-volts ($\mu = 0 \cdot 54$ cm.$^{-1}$). This value is in good agreement with that of Běhounek,[‡] who found $\mu = 0 \cdot 58$

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[*] Part I.

[†] 'Nature,' vol. 131, p. 57 (1933).

[‡] 'Z. Physik,' vol. 69, p. 654 (1931).

cm.$^{-1}$. Since, however, Kolhörster had previously found that the absorption coefficient in iron corresponded to a radiation harder than the ThC″ γ-rays (*i.e.*, $h\nu > 2\cdot6 \,.\, 10^6$ e-volts), it seemed just possible that the absorption coefficient in lead was misleading, being the sum of a small scattering term (corresponding to the high quantum energy) and a large nuclear term. We therefore measured the absorption coefficient in iron also, with the same experimental arrangement as was used for lead. With 1·35 cm. of lead immediately around the chamber, the reduction in intensity produced by an additional 2 cm. of iron corresponded to $\mu_{\text{Fe}} = 0\cdot31$ cm.$^{-1}$ ($h\nu = 2\cdot2 \,.\, 10^6$ volt) which is in satisfactory agreement with the value ($2\cdot0 \,.\, 10^6$) deduced above from the lead absorption coefficient.

It appears that 1 gm. of pure potassium gives the same ionization in our chamber (steel walls 1 cm. thick) as the radiation from $1\cdot6 \,.\, 10^{-11}$ gm. radium, in fair agreement with Běhounek who concluded that the potassium γ-radiation was equivalent to $1\cdot3 \,.\, 10^{-11}$ of the hard γ-radiation of RaC in equilibrium with the same weight of radium. From this value one can deduce that only 3 quanta are emitted for every 100 disintegrating potassium atoms.

The secondary nuclear γ-radiation, excited by ThC″ γ-rays was about 1·5 times the intensity of the natural γ-radiation. The absorption curve was not obtained with great accuracy, but it will be seen from fig. 5 that both as regards quality and intensity it falls into line very well with the other light elements.

Table III.—Analysis of Absorption Curves into Two Components.

	Soft.		Hard.		Initial ionization.
	μ in cm.$^{-1}$.	$h\nu$ in volts.	μ in cm.$^{-1}$.	$h\nu$ in volts.	Hard/Soft.
Carbon	2·0	$0\cdot45 \,.\, 10^6$	—	—	∼0
Potassium			—	—	—
Iron			?	—	0·05
Copper			?	—	0·07
Tin	$2\cdot0_5$	$0\cdot45 \,.\, 10^6$	0·75	$1\cdot1 \,.\, 10^6$	0·14
Lead	$1\cdot9_5$	$0\cdot46 \,.\, 10^6$	0·75	$1\cdot1 \,.\, 10^6$	0·32

Carbon, Iron, Tin, Lead—Excited by RaC γ-rays.—The absorption curves of these radiations, fig. 7, show a very marked general resemblance to the curves of fig. 5, representing the radiations excited by the ThC″ γ-rays, in that there is a progressive increase in the relative amount of hard radiation with increasing atomic number. Our previous measurements with a radon source were confined to an examination of the secondary radiation from lead, and that only from 1·3 cm. absorber onwards, from which it appeared that the radiation was the same as that excited by ThC″ γ-rays. While these observations have been essentially confirmed, a study of the early part of the absorption curve shows unmistakably the presence of radiation which is softer than any excited by ThC″ γ-rays—not only from lead, but from tin and iron, and probably also from carbon. Any hypothesis of the type suggested in our former paper leads one to expect that the radiation excited by RaC γ-rays will differ from that excited by ThC″ γ-rays only by the presence of a small intensity of a very soft component. With this expectation in mind, it was found that our curves could be analysed into three components, two of which are identical with the ThC″ excited radiations, and in the same proportion, and a third which is somewhat softer in light than in heavy elements and has a quantum energy of about 0·35 . 10^6 volts. Thus lead, for example, might consist of the three components

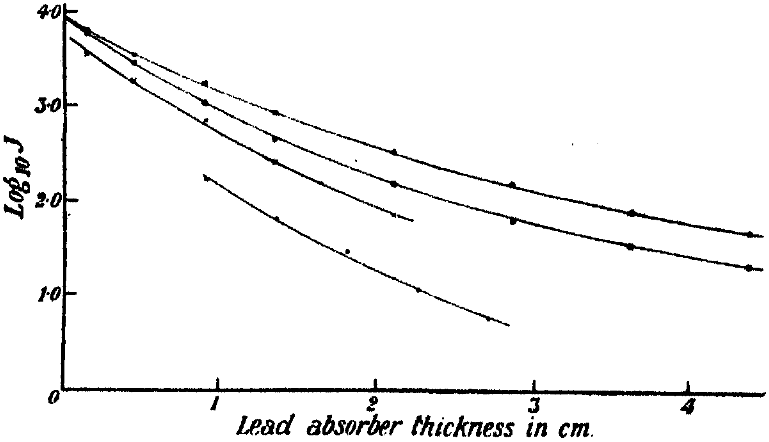

Fig. 7.—Emission at 125° excited by radium C γ-rays. ⊙, lead; ⊡, tin; ×, iron; ●, coal.

$$\mu_{Pb} = 2\cdot2 \text{ cm.}^{-1} \qquad \mu_{Pb} = 2\cdot0 \text{ cm.}^{-1} \qquad \mu_{Pb} = 0\cdot75 \text{ cm.}^{-1}.$$

We find, however, that the energy emitted in the form of the softest component is approximately equal to that of the sum of the other components, and we shall see later that this fact compels us to abandon the hypothesis discussed in the earlier paper.

Without *a priori* reasons to the contrary, it is natural to attempt to analyse the curves into two components only. This is possible, within our limits of error, for all four elements, as shown in Table IV.

Table IV.

	Soft.		Hard.		Initial ionization.
	μ in cm.$^{-1}$.	$h\nu$ in volts.	μ in cm.$^{-1}$.	$h\nu$ in volts.	Hard/Soft.
Carbon	(2·6)	—	(0·75)	—	~ 0
Iron	2·6	$0{\cdot}38 \,.\, 10^6$	(0·75)	$(1{\cdot}1 \,.\, 10^6)$	$0{\cdot}04_8$
Tin	2·4	$0{\cdot}40 \,.\, 10^6$	0·75	$1{\cdot}1 \,.\, 10^6$	$0{\cdot}06_0$
Lead	2·1	$0{\cdot}44 \,.\, 10^6$	0·75	$1{\cdot}1 \,.\, 10^6$	$0{\cdot}12_5$

The first centimetre of the absorption curve for carbon is somewhat uncertain owing to the difficulty of estimating the Compton scattering. Between 1 and 3 cm. the curve is approximately parallel to that for iron (mean $\mu = 1{\cdot}9$ cm.$^{-1}$) so that the secondary radiations from these two elements must be very similar.

A further point of interest is that, at each absorber thickness, the ratio of the ionizations observed with lead and tin is the same with the radon as it is with the radiothorium radiations. In a similar way the ratio lead/iron and lead/carbon is also the same for both primary radiations. Since the absorption coefficients of the secondary radiations vary only slightly with changes in the exciting radiation, this presumably indicates merely that the variation with atomic number of the intensity of emission of the soft and of the hard components of the secondary radiation is independent of the quantum energy of the exciting radiation.

§ 5. *The Quantum Energy of Radiation Undergoing Nuclear Interaction.*

The experiments of Chao[*] suggested the existence of a " threshold " quantum energy for nuclear interaction at about $2 \,.\, 10^6$ e-volts. If we make the assumption that on the high energy side of the threshold the nuclear interaction coefficient is constant, it is possible to obtain an estimate of the position of such a threshold from a comparison of the intensity of the nuclear radiation excited by RaC and ThC″ γ-rays. The procedure was explained in detail in

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[*] 'Proc. Roy. Soc.,' A, vol. 135, p. 206 (1931).

Part I, where it was shown that our experimental results were in agreement with the above value $h\nu_e = 2 \cdot 10^6$ e-volts.

It was also pointed out that, on the basis of the same assumption, a value of $h\nu_e$ could be obtained from the apparent absorption coefficient of the primary radiation measured by introducing an absorber between the source and the radiator. In the present experiments the shape of the absorber, fig. 8, was such that rays traverse it approximately perpendicularly. The variation of the "primary absorption coefficient" with the thickness of lead surrounding the ionization chamber is shown in fig. 9. Considering first the apparent absorption coefficient of the ThC$''$ γ-rays, we see that the value falls rapidly at first. The large initial value is due to the fact that, with no lead round the chamber, a considerable part of the ionization is due to Compton scattered radiation, some of which is derived from the softer components of the ThC$''$ spectrum. As would be expected, the value is highest for the carbon radiator and least for lead, corresponding to the relative proportions of Compton and nuclear radiation from these elements.

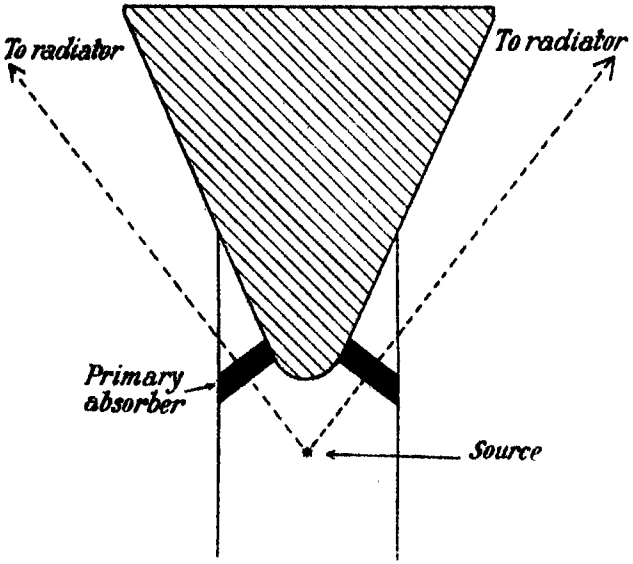
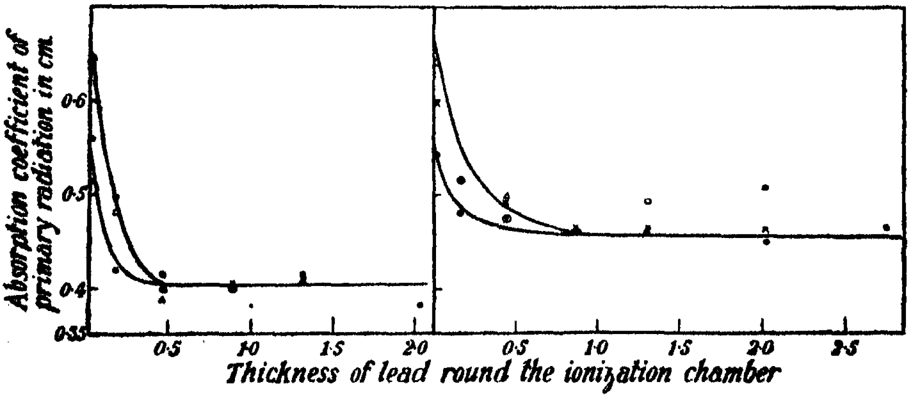


FIG. 8.

The Compton radiation is rapidly absorbed as the thickness of lead round the chamber is increased, and the primary absorption coefficient reaches the constant value $0 \cdot 40_6 \pm 0 \cdot 009$ cm.$^{-1}$—which it will be observed is actually smaller than the true absorption coefficient $0 \cdot 46_5$ cm.$^{-1}$ of the hard line

($h\nu = 2 \cdot 6 \,.\, 10^6$ e-volts). The low value is easily seen to be due to the fact that some of the scattered radiation from the primary absorber, though of greater wave-length than the primary rays, is still of sufficiently large quantum energy to undergo nuclear interaction. If we assume that the softer components of the ThC″ spectrum do not interact *at all*, the difference between the true and observed absorption coefficients indicates the angular range (21°) of scattered radiation which interacts, and hence the position of the threshold. The above values lead to $h\nu_0 = 1 \cdot 98 \,.\, 10^6$ e-volts (limits $1 \cdot 74$ and $2 \cdot 06 \times 10^6$ e-volts). As a check, the primary absorption coefficient was also measured in iron, with 0·45 cm. and 1·35 cm. of lead round the chamber. The observed values were $\mu_0 = 111$ and 107×10^{-27} respectively, which, compared with the true value, 134×10^{-27}, lead to $h\nu_0 = 1 \cdot 85 \,.\, 10^6$ e-volts.



(*a*) (*b*)

FIG. 9.—(*a*) radiothorium source; (*b*) radon source; ●, lead; ×, tin; ○, iron; △, carbon radiators.

Interaction of the Soft Components.—The softer γ-rays emitted by the radiothorium source have a quantum energy less than $0 \cdot 8 \,.\, 10^6$ e-volts, and $\mu_{Pb} > 1 \cdot 5$ cm.$^{-1}$, so that if these rays contributed at all to the secondary emission, their influence on the primary absorption coefficient would be very marked. Allowing the maximum possible reduction in the absorption coefficient of the hard lines due to scattering, as explained above, and taking into account the relative intensity of the softer components we estimate that the probability of interaction is not greater than 15% of that of the hard lines, so that the absorption coefficient for this process is not greater than 0·015 cm.$^{-1}$.

Radon Source.—The observations, fig. 9, of the absorption coefficient of the radon rays may be treated similarly, though with these the matter is a little more complex in that there are a number of hard components which may be taking part. Table V shows the absorption coefficients to be expected if the threshold is just less than the values indicated.

Table V.

Quantum energy (10^6 ε-volts)	2·65	2·21	1·93	1·78
Effective absorption coefficient (cm.$^{-1}$ lead)	0·405	0·448	0·471	0·539

It will be seen that these observations afford a fairly sensitive test of the value of $h\nu_0$ and again lead to a value $2 . 10^6$ ε-volts.*

We also obtain as an upper limit for the participation of the softer components the interaction coefficients $\kappa < 0\cdot004$ cm.$^{-1}$ and $\kappa < 0\cdot006$ cm.$^{-1}$ in the neighbourhood of $1\cdot3$ and $0\cdot6 . 10^6$ ε-volts respectively. These coefficients of course refer to any type of interaction leading to the re-emission of the absorbed energy as a secondary γ-radiation, and therefore include coherent (classical) scattering by the orbital electrons.

The curves of figs. 9, *a* and *b*, show two further points of considerable interest :—

(1) The absorption coefficient is the same within the limits of experimental error, for all four elements, from which follows the very remarkable fact that the threshold energies of these elements do not differ by more than $0\cdot1 . 10^6$ ε-volts.

(2) The primary absorption coefficient does not vary with the thickness of absorber round the chamber. Considering the radiation excited by the complex RaC γ-rays it is clear that since the relative proportions of the hard and soft components of the secondary radiation change greatly (from 20% hard at 0·6 cm. to 90% hard at 3 cm.) this constancy implies that all the primary quanta excite both components in about the same proportion.

§ 6. *Conclusion.*

All the elements so far studied, viz., C, O, K, Cu, Fe, Sn, and Pb, have been found to emit a comparatively soft secondary γ-radiation when irradiated by the hard γ-rays either of ThC″ or RaC. The quality of the secondary radiation has been studied by absorption methods, using, in general, lead absorbers. Since the quantum energy of the secondary radiation is below the threshold for nuclear interaction, the interpretation of the absorption coefficients is not influenced by the phenomenon under observation (anomalous absorption). As a check, however, the absorption of the secondary lead radiation was also measured in iron, with results entirely in accord with the previous measurements using lead absorbers.

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* Naturally, the value of $h\nu_0$ derived from these considerations depends on the particular assumption regarding the variation of the nuclear absorption coefficient with wavelength. Thus if $\kappa \propto (\nu - \nu_0)^4$, then $h\nu_0 \sim 1\cdot0 . 10^6$ ε-volts.

The absorption curve of the ordinary Compton scattered radiation (at 125°) was calculated, and was also determined experimentally with a carbon radiator.

We have also shown that the particular experimental arrangement employed is a very suitable one, since by the application of small corrections (representing a change in absorption coefficient of only 5%), logarithmic absorption curves are obtained, such that the gradient at any point represents the true absorption coefficient of the radiation under investigation.*

Radiation Excited by ThC″ γ-rays, fig. 5.—It appears that in every case at least two-thirds of the total secondary γ-ray energy is emitted in the form of a soft radiation having a quantum energy of the order of $0 \cdot 5 \, . \, 10^6$ volts. With lead, the remaining third of the emission is in the form of harder radiation. Within the limits of experimental error the absorption curve can be analysed into two monochromatic components :—

$$\mu_S = 2 \cdot 0 \text{ cm.}^{-1} \qquad \mu_H = 0 \cdot 75 \text{ cm.}^{-1}$$
$$h\nu_S = 0 \cdot 45 \, . \, 10^6 \text{ e-volts.} \qquad h\nu_H = 1 \cdot 1 \, . \, 10^6 \text{ e-volts.}$$

While it is not possible, by absorption methods, to decide conclusively between discrete lines and comparatively wide spectral bands it is certain that the secondary emission must comprise considerable concentrations of energy in the form of radiation having absorption coefficients in the neighbourhood of the values given. As we pass from lead to elements of lower atomic number the proportion of hard radiation rapidly decreases. Correspondingly there is greater uncertainty in the absorption coefficient of this component, and greater accuracy in the estimation of that of the soft com-

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[*] In gathering together the information which appears to be established concerning the nature of the secondary γ-ray emission accompanying the "anomalous absorption" of high energy γ-radiation, we are able, through the kindness of a Professor Stahel, to include many references to the results of a parallel investigation by Stahel and Ketelaar ('C. R. Acad. Sci. Paris,' vol. 196, p. 1664 (1933)), a full account of which will be found in the 'J. Phys. Rad.'

ponent. There is still definite evidence of the presence, in iron and copper, of a small intensity of a hard component, though its absorption coefficient could only be given within comparatively wide limits. It will be seen from the curves, fig. 5, however, that the soft component is very closely the same for all elements—for C, K, Cu, Fe, and Sn the quantum energy of this component can hardly differ by more than a few per cent.

There is no evidence, from the absorption curves, of the presence in appreciable intensity, of radiation harder than about $1 \cdot 0 \,.\, 10^6$ volts. On account of the theoretical importance of any unmodified scattering of the incident high energy radiation from thorium C″ this matter has been examined very carefully. Since the ordinary secondary emission from carbon consists almost entirely of the soft component it is possible to tell very accurately whether any unmodified radiation is present, and it appears that less than 1% of the total emission from carbon is of such unmodified radiation. The corresponding limits for lead are naturally much greater. A special experiment* was therefore devised for this element, which enabled us to satisfy ourselves that not more than 2% of the total emission, for lead, was in the form of radiation of primary hardness.

The absolute values of the quantum energy, of course, depend on the accuracy of the $\mu - \lambda$ curve, but for reasons already discussed we believe they are almost certainly correct to 10%.

Radiation Excited by RaC γ-rays, fig. 7.—The elements C, Fe, Sn, and Pb when irradiated with RaC γ-rays gave a secondary emission similar to, but not identical with, that excited by ThC″ γ-rays. The hard component does, in fact, appear to be the same with the two sources, but the soft components differ. For lead, the soft component excited by RaC γ-rays may either be a little softer, or it may be present in greater proportion than in the ThC″ secondary radiation. The soft component of the radiation from other elements (Sn, Fe, C) is definitely somewhat softer when excited by RaC γ-rays, and is also present in greater relative intensity. The difference in quantum energy between the soft components excited by RaC and ThC″ γ-rays is of the order of $0 \cdot 1 \,.\, 10^6$ volts.

On account of the difficulty of analysing absorption curves it is hardly possible to say more than that, when excited by RaC γ-rays, all the elements examined give a secondary emission having a peak intensity in the region $0 \cdot 35$–$0 \cdot 45 \,.\, 10^6$ volts ($\mu_{Pb} = 3 \cdot 0 - \mu_{Pb} = 2 \cdot 0$ cm.$^{-1}$), and that heavy elements

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* Part I, p. 689. In this experiment the region 90°–150° only was investigated. The limits given assume an isotropic distribution.

(Pb and Sn) give in addition a relatively weak radiation (15% and 7% respectively of the total energy) having a peak intensity at about $1 \cdot 1 \,.\, 10^6$ volt.

If, however, a particular intensity distribution were proposed on theoretical grounds it could be tested very readily and accurately by the experimental curves.

These results appear at first sight to be at variance with those of Meitner and Hupfeld,[*] since these authors state that the secondary radiation has the same hardness as the primary radiation. It is at once apparent, however, that since they examined the secondary emission at 90° where the quantum energy of the Compton scattered radiation is $0 \cdot 4 \,.\, 10^6$ volts a soft component of nuclear radiation having a peak intensity at about $0 \cdot 45 \,.\, 10^6$ volts could only be distinguished with difficulty from Compton radiation. In confirmation of this, it appears to us that the observed ratio (2 : 1) of the intensity of the radiation from equi-dimensional blocks (3 cm. cube) of iron and lead radiators, is considerably smaller than it should have been (on account of reabsorption) indicating that some of the soft radiation from lead was of a different origin. With regard to the hard component, observed by both Meitner and Hupfeld and ourselves, there appears to be reasonable agreement as regards the *intensity* of this component, but a difference in the estimated absorption coefficient of $0 \cdot 2$ cm.$^{-1}$. Having regard to the exact analytical considerations of § 3 (*c*), where we took as the extreme limits of error 2% at each of four points, and 3% at the last point on the absorption curve, extending over a range of 4 cm. of lead, we feel confident from our measurements that the true value of the absorption coefficient[†] lies within the limits

$$0 \cdot 65 < \mu < 0 \cdot 85 \text{ cm.}^{-1}.$$

Since Meitner and Hupfeld's curve extended only to 3 cm. of absorber and the final points were subject to a probable error of 20% (on account of a large background due to penetrating radiation) the same analytical considerations make it difficult to be certain that the radiation is of primary hardness, $\mu = 0 \cdot 54$ cm.$^{-1}$, and not within the above range.

On the other hand, the results of Stahel and Ketelaar (*loc. cit.*), who attained considerable accuracy by the use of a high pressure ionization chamber and a large source (1·6 gm. radium) are essentially in agreement with our own. They find the following components, for lead,

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[*] 'Z. Physik,' vol. 75, p. 705 (1932).

[†] As before, this coefficient may not imply a single line, but the centre of gravity of a relatively wide band of energy.

$$\mu_S = 2\cdot1 \text{ cm.}^{-1}, \qquad \mu_H = 0\cdot90 \text{ cm.}^{-1},$$

and, as in our experiments, the mean hardness of the secondary radiation was observed to decrease with decreasing atomic number.

Stahel and Ketelaar have made the further important observation that the nuclear radiation from lead does not change in hardness as the angle of emission changes from 80°–95°–130°–135°. Combining this with our previous observation that the radiation is the same at 125° and 140°, and our new observations at 175°, we see that there is every indication that the quality of the secondary radiation is independent of the angle of emission. The observations from 80°–145° refer to the whole of the radiation excited in lead by RaC γ-rays, and those at 175° to the soft component only, excited in light elements, by both RaC and ThC″ sources.

By measuring the apparent absorption coefficient of the primary radiation Stahel and Ketelaar conclude that only the hard components of the RaC spectrum are giving rise to any appreciable secondary emission. Our own measurements support this conclusion, setting the threshold (if a sharp threshold exists) at $1\cdot9$–$2\cdot1 \, . \, 10^6$ volts.

It appears, moreover, that radiation of the order of $1\cdot3$ and $0\cdot6 \, . \, 10^6$ volts does not give rise to any type of secondary emission (as, for example, "classical scattering") other than Compton scattered radiation, to a greater extent than is represented by the interaction coefficient $\kappa = 0\cdot005$ cm.$^{-1}$, or 5% of the anomalous absorption of the $2\cdot6 \, . \, 10^6$ volt radiation.

Attempts to Interpret the Observations in terms of Nuclear Structure.—A number of theoretical explanations have been attempted,* all of which have in common the assumption that the function of the incident radiation is to excite (or ionize) some structural unit of the nucleus which subsequently emits a "characteristic radiation." We pointed out in our former paper that such an hypothesis might, with suitable additional hypotheses, be made to account for the secondary radiation excited by ThC″ γ-rays—though not without arbitrariness, in that it did not account for the impossibility of exciting the nucleus by half-million volt radiation. The following considerations appear to show that there is definite experimental ground for rejecting any such hypothesis.

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* Heisenberg, 'Z. Physik,' vol. 77, p. 1 (1932); vol. 78, p. 156 (1932); Arakatzu, 'Mem. Taihoku Imp. Univ.,' vol. 5, p. 163 (1932); Gamow, 'Nature,' vol. 131, p. 57 (1933); Beck, 'Kernbau u. Quanten mechanik,' "Handb. d. Radiologie" (1933).

If the excitation is occasioned by radiation having a higher quantum energy than the excitation potential of the interaction process ($\sim 2 \,.\, 10^6$ volts) the excess energy should be emitted as " Raman scattered " radiation. Thus the energy of this Raman scattered radiation should vary considerably as the incident radiation is changed from ThC″ to RaC, the mean values being respectively $(2{\cdot}60\text{–}2{\cdot}0) \,.\, 10^6$ volts and $(2{\cdot}2\text{–}2{\cdot}0) \,.\, 10^6$ volts. It would be just possible to allow that a Raman scattered component of $0{\cdot}6 \,.\, 10^6$ volts was present in the ThC″ excited radiation of all elements, and we have seen that the radiation excited RaC might contain an additional soft component having a quantum energy of about $0{\cdot}3 \,.\, 10^6$ volts. It is a necessary consequence of the hypothesis, however, that this radiation should be very weak (viz., $0{\cdot}2/2{\cdot}6$ or 8% of the emission) whereas in our measurements it represents nearly half the total emission.

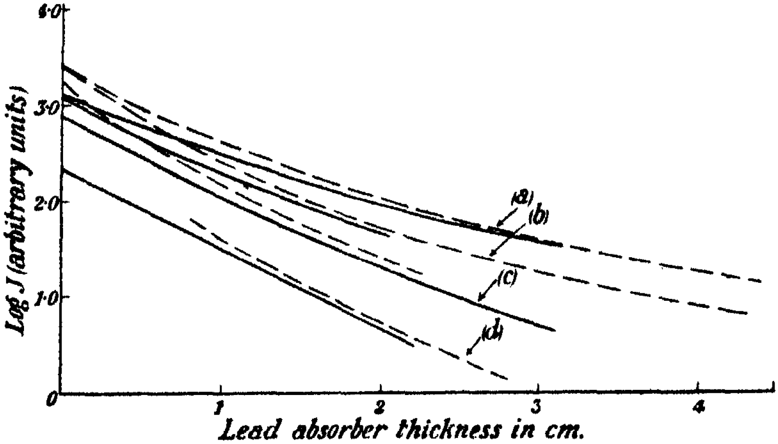

FIG. 10.—Comparison of the radiations excited by ThC″ and RaC γ-rays. (*a*) lead; (*b*) tin; (*c*) iron; (*d*) carbon. —— radio thorium source; – – – radon source.

Considering the possibilities of experimental error we see at once from figs. 5 and 7 that the discrepancy cannot be due to random errors of the individual measurements. Moreover, it cannot arise in the correction of the curves to standard conditions, since the curves which we are comparing represent closely similar radiations, and therefore the corrections (which are small) are also nearly identical. There remains only the correction for Compton scattered radiation; apart from the fact that this correction is based on experiment (see

§ 3 (*a*)) it is clear that it cannot be responsible for the difference between the two curves, *for two reasons:* (*a*) the departure of the RaC from the ThC″ curves is still quite apparent at 2 cm. of absorber, where the Compton radiation only accounts for 0·02% of the observed ionization with a lead radiator, and (*b*) since the nuclear emission varies as Z^2, an error in the estimation of the Compton scattering will affect light and heavy elements to very different extents, whereas the $0 \cdot 3 . 10^6$ volt component of the RaC secondary radiation represents approximately the same proportion of the emission from all elements.

Since we can find no real ground for doubting that the experimental curves correctly represent the difference between the secondary radiations excited by the RaC and ThC″ γ-rays, it appears necessary to abandon any hypothesis which implies that the major portion of the emission is a "characteristic radiation" of the absorbing system.

Phenomena Associated with the Anomalous Absorption of High Energy Gamma Radiation.—III.

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(Communicated by Lord Rutherford, O.M., F.R.S.—Received November 7, 1933.)

§ 1. *Introduction.*

In the previous paper we have presented the results of certain experiments on the absorption of the secondary γ-radiation emitted by atomic nuclei when irradiated with very high energy γ-radiation. We now proceed to discuss the conclusions which may be derived from these results regarding the proportion of the γ-ray energy absorbed by a nucleus which is emitted by it as radiation having a smaller quantum energy.

There are also presented some new experimental results concerning the isotropic distribution of this radiation, together with an account of certain other experiments designed to throw some light on the mechanism of this interaction. Before these points are considered, however, it seemed worth while, in view of the inadequacy of any theoretical interpretation of the phenomenon, to make quite certain that the secondary radiation was really a γ-radiation.* For this purpose the following experiments were carried out.

§ 2. *Evidence that the Secondary Emission is really a γ-radiation.*

(*a*) *Comparison of Ionization in Nitrogen and Hydrogen at the same pressure, 80 atmospheres.*—This ratio was determined experimentally and found to be $N_2/H_2 = 4 \cdot 5$ for both hard and soft components of the secondary nuclear radiation—in good agreement with the value 4·4 obtained with a γ-ray beam of the same mean wave-length. This shows that very little, if any, of the radiation which we have been observing could be due to neutrons for which the ratio is known experimentally to be about 0·3.

(*b*) *Wilson Chamber Photographs.*—A Wilson chamber was irradiated by the secondary γ-radiation from lead in such a way that 10^6 ion pairs must have been produced in the air in the chamber during the period of photography. The tracks observed gave no evidence for the presence of any radiation other than the γ-radiation referred to in Part II.

§ 3. *The Fraction of the γ-ray Energy Absorbed by a Nucleus and Re-emitted as Secondary Radiation.*

The above experiments indicate that the secondary emission is mainly, if not completely, a γ-radiation, and, on this assumption, we may now proceed to compare the total energy emitted as secondary radiation with that absorbed, *i.e.*, with the quantum energy of the incident high frequency radiation.

The fraction of the incident γ-ray energy which is re-radiated by each nucleus, ${}_{N}\kappa_{\gamma}$, can be evaluated by simple geometric considerations if the ratio of the intensities of the incident γ-ray energy at the radiator to that of the secondary radiation at the ionization chamber is known.

This ratio, ${}_{N}\kappa_{\gamma}$, of the γ-ray intensities can be obtained from the observed ratio in the ionizations $I_{(\text{direct})}$ and $I_{(\text{secondary})}$ at the two points respectively by multiplying by the appropriate change in "ionization function."† In the exact calculation due attention is paid to the effect of the size of the radiator, and the total value of ${}_{N}\kappa_{\gamma}$ will be the sum of contributions from the hard and from the soft components, so that the intensities and absorption coefficients of these two components must be found in the manner discussed in our previous paper. The final value of the sum will not be greatly affected by errors in the analysis of the absorption curve, since, if the one component is overestimated, the other will necessarily be underestimated to approximately the same extent.

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* The fact that Meitner and Hupfeld have observed a small part (the hard component) of the secondary emission with a γ-ray counter, makes it very probable that some γ-radiation is present, but gives no information concerning the nature of the main emission at 125°.

† The ionization produced by an equal energy flux of the two radiations under consideration.

The main difficulty in the determination of ${}_N\kappa_\gamma$ by the above method occurs in the determination of $I_{(direct)}$ (*i.e.*, the γ-ray intensity at the radiator) since this quantity refers only to those lines ($h\nu > 2 \cdot 0 \, . \, 10^6$ e-volts) taking part in the interaction.

It is a very difficult matter to filter all of the soft components from the beam of thorium C″ γ-radiation without introducing uncertainties caused by radiation scattered from the walls of the room or from the sides of the canalizing system. Since 6 cm. of lead are necessary for the filter, an additional difficulty is to make certain that no radiation scattered by this filter enters the ionization chamber.

A second difficulty in the determination of ${}_N\kappa_\gamma$ lies in the uncertainty regarding the homogeneity of thorium C″ γ-radiation, since subsidiary γ-ray lines at $2 \cdot 05$ and $1 \cdot 65 \times 10^6$ e-volts have been found by Skobelzyn[‡] in an intensity of 10% of the total hard radiation and have been corroborated by Alexander.[§] Although the latter of these components will, presumably, have too low an energy to contribute to this secondary emission, it will still be present, though with diminished intensity, in our measurement of $I_{(direct)}$. Thus if this particular line is really present in the beam the values of ${}_N\kappa_\gamma$ for the hard and soft components of the secondary emission given in Table I should all be increased by about 4%.

Table I.

Element.	Lead.	Tin.	Copper.*	Iron.	Carbon.†
Z	82	50	29	26	6
Hard component ${}_N\kappa_\gamma$ 10^{+27}	485	99	15·1	10	0
Soft component ${}_N\kappa_\gamma$ 10^{+27}	2670	950	315	282	19·2
Total ${}_N\kappa_\gamma \times 10^{+27}$	3155	1049	330	292	19·2
Total fraction absorbed ${}_N\kappa$ by the nucleus $\times 10^{+27}$	2860	860	298	258	21
Ratio ${}_N\kappa_\gamma / {}_N\kappa$	1·1	1·2	1·1	1·1	0·9
$\frac{{}_N\kappa_\gamma}{Z^2} \times 10^{27}$	0·47	0·42	0·39	0·43	0·53

* Less accurate as the geometry of the radiator was uncertain.
† Less accurate.

[‡] 'C. R. Acad. Sci. Paris,' vol. 194, pp. 1486, 1568 (1932).

[§] Unpublished results (Cavendish Laboratory).

The uncertainty regarding the homogeneity of the thorium C″ γ-radiation mentioned above will hardly affect the values of the total nuclear absorption coefficient ${}_{\mathrm{N}}\kappa$ as deduced from absorption measurements, because it happens by chance that the weighted mean value of the photoelectric absorption of the two subsidiary lines—being greater than that of the 2·62 line—just balances the absence of the nuclear absorption in the softest line.

In our preliminary paper the fraction ${}_{\mathrm{N}}\kappa_{\gamma}/{}_{\mathrm{N}}\kappa$ was found to be about 0·53—a value much smaller than that found above. About one-half of the difference between ${}_{\mathrm{N}}\kappa_{\gamma}$ published in our first paper and those given here is due to the errors in the determination of $\mathrm{I}_{(\mathrm{direct})}$, while the remaining part of the difference is due to the fact that in these early measurements the source was so near the base of the lead shielding cone that this absorbed some of the radiation going to the radiators. These errors occurred in the absolute determination of the fraction ${}_{\mathrm{N}}\kappa_{\gamma}$ only, and did not affect its variation with atomic number.

No importance should be attached to the fact that some of the ratios ${}_{\mathrm{N}}\kappa_{\gamma}/{}_{\mathrm{N}}\kappa$ are greater than unity, since the determinations of both ${}_{\mathrm{N}}\kappa_{\gamma}$ and ${}_{\mathrm{N}}\kappa$ are subject to errors of this order of magnitude. The closeness of the ratio to unity does, however, indicate that if the radiation is distributed isotropically the process of the interaction is essentially one involving the degradation of radiation, four to six quanta of low energy being emitted for each high energy quantum absorbed. The lower ratio obtained with carbon is probably due to an error in ${}_{\mathrm{N}}\kappa_{\gamma}$ caused by uncertainty in the analysis of the absorption curve into nuclear and Compton scattered components, or caused by the influence of the radiation scattered by the walls of the room. The value of ${}_{\mathrm{N}}\kappa$ is also in considerable doubt for this element since it is very small compared with the fraction absorbed in the normal processes.

As shown in Table II the total intensity of the hard component alone varies approximately as Z^3.

Table II.

	Fe.	Cu.	Sn.	Pb.
$\dfrac{{}_{\mathrm{N}}\kappa_{\gamma}\ \text{hard component}}{Z^3} \times 10^{31}$	5·8	6·2	8·0	8·9

§ 4. *The Magnitude of the Interaction as a Function of the Atomic Number.*

The figures given in the last line of Table I are approximately constant and show that the nuclear interaction varies roughly as the square of the atomic number. In order to ascertain more accurately if any such simple power law is really valid the values of ${}_{N}\kappa_{\gamma}$ are plotted logarithmically against the atomic number in fig. 1, in which the lengths of the vertical line represent the limits (and not the probable error) of error of the measurements.

It will be seen from this figure that a variation proportional to $Z^{2\cdot0}$ fits the experimental data and that a value of the exponent higher than 2·1 or lower than 1·8 seems definitely precluded in view of the relatively large nuclear effect with carbon. As has already been indicated the value obtained with carbon is much less accurate than the corresponding results with lead, tin, and iron, but it is most unlikely that the value of ${}_{N}\kappa_{\gamma}$ for carbon can lie outside the limits given in fig. 1. This decrease in accuracy arises from the fact that any uncertainty regarding the amount of the radiation scattered from the walls of the room and intercepted by the radiator before reaching the ionization chamber, will be much greater relatively when the nuclear effect is small. A further reason for the diminished accuracy is that radiation which is Compton scattered by the radiator is determined entirely by analysing the absorption

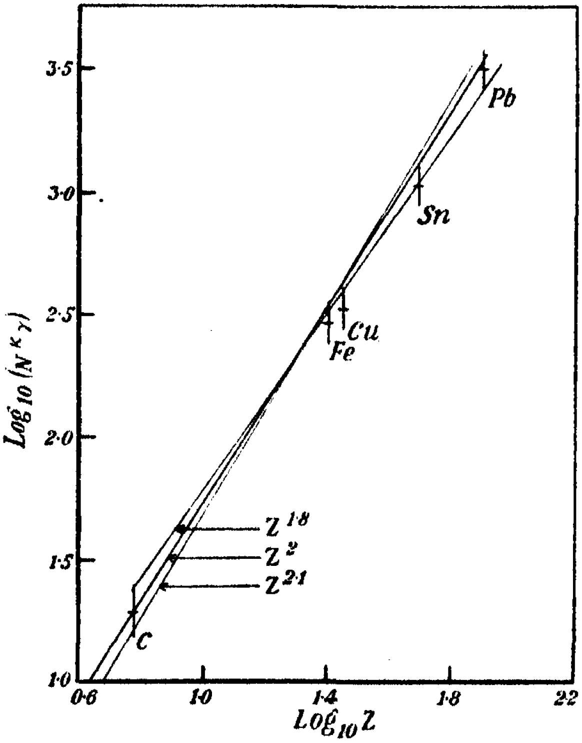

FIG. 1.—Variation of ${}_{N}\kappa_{\gamma}$ with atomic number.

curve of carbon into a very soft Compton scattered component and a harder nuclear component. This possible error is not so great as might be expected, however, since we can justifiably assume that the absorption coefficient of the nuclear radiation is the same as that found for the other light elements, when excited by thorium C″ γ-radiation.*

Further information concerning the variation of the nuclear interaction with atomic number may be obtained from the results† of the published absorption experiments of the thorium C″ γ-radiation. Since the total absorption coefficient is $(\sigma_e + \tau_e + {}_e\kappa)$, we may determine ${}_e\kappa$ by subtracting the sum of σ_e and τ_e. While τ_e for lead can be obtained to a 10% accuracy from Gray's‡ empirical and experimental law, we have no real experimental evidence for our belief that it will vary with the cube of the atomic number, for this high energy radiation. This uncertainty in τ_e is, however, not so serious as it appears, since with elements of high atomic number the total nuclear interaction is certainly three or four times the photoelectric effect.

A further possibility of inaccuracy in the estimation of ${}_e\kappa$ occurs in connection with the determination of σ_e which is found from the experimental value of the absorption coefficient for light elements (such as carbon) by the subtraction of ${}_e\kappa_\gamma$ as determined above. (This is justifiable since we know that ${}_e\kappa_\gamma$ is of the same order of magnitude as ${}_e\kappa$.) The Klein-Nishina formula is only strictly applicable to free electrons and some slight alterations in σ_e might possibly be expected for the bound and rapidly moving K electrons in heavy elements. For the lighter elements, however, the value of σ_e obtained in this way is $123 \cdot 5 \times 10^{-27}$ and appears to have upper and lower limits of $122 \cdot 7$ and $124 \cdot 2 \times 10^{-27}$ respectively. This is in very good agreement with the theoretical value of $123 \cdot 5 \times 10^{-27}$ calculated for the quantum energy of $2 \cdot 620 \times 10^6$ e-volts, and the spectroscopic value for e/m_0. If, however, the additional γ-ray lines at $1 \cdot 65$ and $2 \cdot 05 \times 10^6$ e-volts found by Skobeltzyn are included the theoretical value would be raised to $125 \cdot 5$ and $128 \cdot 6 \times 10^{-27}$ respectively. It thus appears that these lines can only be present in the intensity found by Skobeltzyn if the value of σ_e is reduced by the presence of a considerable intensity of a much harder component of radiation than has hitherto been observed.

When all of these inaccuracies are taken into consideration the information obtained concerning the variation of ${}_N\kappa$ with atomic number is somewhat less accurate than that for ${}_N\kappa_\gamma$ possibilities ranging between a variation per nucleus proportional to $Z^{2\cdot 25}$ and $Z^{1\cdot 75}$ being allowed.

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* See, however, footnote to p. 686, part II.

† Tarrant, 'Proc. Roy. Soc.,' A, vol. 135, p. 223 (1932).

‡ 'Proc. Camb. Phil. Soc.,' vol. 27, p. 103 (1931).

§ 5. *The Value of ${}_N\kappa_\gamma$ for the Radium Radiation.*

Owing to the complexity of the RaC γ-ray spectrum and the absence of any definite information concerning the variation of the interaction with the wave-length it is most convenient to assume—in order to obtain figures which can conveniently be compared with those of other experimenters—that the whole of the high energy component of the RaC spectrum is effective (*i.e.*, that radiation which penetrates 6 cm. of lead and has an absorption coefficient of 0·54 cm.$^{-1}$ in lead).

On this assumption we deduce from our results that ${}_N\kappa_\gamma$ for the hard component of the secondary emission is 132×10^{-27} and for the soft components is 1880×10^{-27}, so that the total ${}_N\kappa_\gamma$ is 2000×10^{-27}. This value for the hard component is in agreement as to order of magnitude, only, with the estimates of Meitner and Hupfeld* (500×10^{-27}), who, however, find, as has already been discussed, that the absorption coefficient of this radiation is somewhat different from our results. These authors did not investigate the soft components of the radiation, but this has been done by Stahel and Ketelaar,† who find the total value of ${}_N\kappa_\gamma$ to be 1700×10^{-27}, and are thus also in agreement with our results.

§ 6. *Evidence concerning the Isotropic Distribution of the Secondary Radiation.*

Since all of the above estimates of ${}_N\kappa_\gamma$ turn entirely on the assumption that the secondary radiation is emitted with the same intensity in all directions, and since the accuracy of this assumption might well be of considerable theoretical importance, we have examined this question in more detail. Our information on this matter is based on a variety of different results, which are each subject to considerable experimental error, but which, taken together, make it certain that the radiation is emitted in at least an approximately isotropic manner.

Stahel and Ketelaar, in the investigation just referred to, found the total value of ${}_N\kappa_\gamma$ at 135° to be 1690×10^{-27} while at 95° the value was 1480×10^{-27}.

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* 'Z. Physik,' vol. 75, p. 705 (1932).

† 'C. R. Acad. Sci. Paris,' vol. 196, p. 1664 (1933), and 'J. Phys. Rad.,' *unpublished*.

Thus at these two angles the intensity of the secondary radiation produced by the radon γ-rays is the same within the errors of the calculation.

The first evidence published on this subject for thorium radiation was by Chao,* who found that the angular distribution was approximately isotropic. He determined experimentally the total scattering from lead and aluminium at a series of different angles, and from his results the rough values, in Table III, of the nuclear scattered intensity can be deduced.

Table III.

Angle	35°	55°	90°	135°
Intensity	0·05	0·06	0·07	0·08

Table III makes it clear that the excess scattering from lead is emitted in about the same intensity in all directions.

In our earlier investigation we found that the absorption curve of the radiation emitted at 145° was identical, within the limits of experimental error, with that at 125°. Thus this change in angle did not affect either the absorption coefficients of the two components or their relative intensity.

Angular Distribution between 64° *and* 114°.—We have investigated this question with the special experimental arrangement shown in fig. 2.

The angle of scattering could be varied between the mean value of 64° and 114° by altering the height of the cylindrical lead radiator. Absorbers were placed directly round the chamber and corrections were made for the oblique incidence of the radiation. The ionization was recorded at three different thicknesses of lead absorber round the chamber, 0 cm., 0·6 cm., and 1·35 cm. respectively and for six different positions of the radiator. The measurements with no absorber were performed merely as a check to make certain that the Compton scatterings of the soft components of the primary radiation were not so large that it could conceivably be of importance in the remaining measurements. Values of the ionization due to the Compton scattering and to the nuclear interaction were calculated theoretically and are compared with experiment in Table IV.

Apart from the value at 114° which is probably too low because some of the secondary radiation was cut off by the lead cone—the values of the ratio experimental/observed with 0·65 cm. of lead round the chamber are a little above unity. This difference is accentuated with 1·3 cm. of lead round the chamber and is therefore presumably due to a wrong value of the "effective thickness" of the lead absorber, or of the value of the absorption coefficient employed. By extrapolating this ratio to zero thickness we eliminate this error and obtain the figures shown in the last row, confirming an isotropic distribution within the limits of 20%. A closer confirmation than this cannot be expected on account of the difficulties in making the calculation.

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* Chao, 'Phys. Rev.,' vol. 36, p. 1519 (1930).

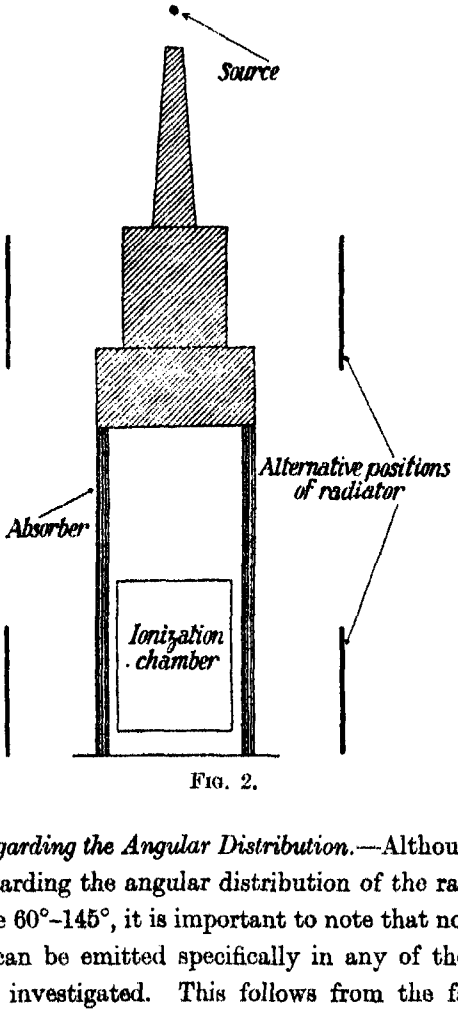

Fig. 2.

General Survey regarding the Angular Distribution.—Although all the evidence discussed above regarding the angular distribution of the radiation refers only to the angular range 60°–145°, it is important to note that no very considerable amount of energy can be emitted specifically in any of the directions which have not yet been investigated. This follows from the fact that we have observed experimentally within this angular range 65% of the total energy absorbed by a nucleus and fig. 3 shows that if the radiation were emitted isotropically a further 35% would just be expected to occur in the other angular regions 0°–60° and 145°–180°.

Table IV.—Thorium C″ γ-radiation. Lead radiator. Ions per cubic centimetre per second.

Mean angle :	114°	94°	84°	78°	69°	64°
Calculated at 0·6 cm. absorber—						
Nuclear	495	555·4	573	571	338	213
Compton	31	77·5	149	276	466	551
Total	526	632·9*	722	847	804	764
Experimental	434	632·9*	822	903	850	754
Ratio	0·82	1	1·14	1·07	1·06	0·99
Calculated at 1·35 cm. absorber—						
Nuclear	154	167	158	139	79	—
Compton	3·8	13·8	30	60	128	—
Total	158	180	188	199	207	—
Experimental	153·8	212·4	275·7	310·3	338·8	—
Ratio	0·98	1·17	1·47	1·55	1·63	—
Extrapolated ratio	0·72	0·89	0·93	0·81	0·76	0·72

* This theoretical value was made exactly equal to the experimental by scaling, since the calculations only gave the variation of the ionization with angle and were not calculated in absolute units.

Thus the only way the isotropic distribution can be altered—if all of the energy absorbed is re-emitted as secondary radiation—is by an increase in the forward direction, for example, being compensated by a decrease in the other (backward) part of the angular range. That no marked alteration in the emission can occur in these directions is shown by the experiments of

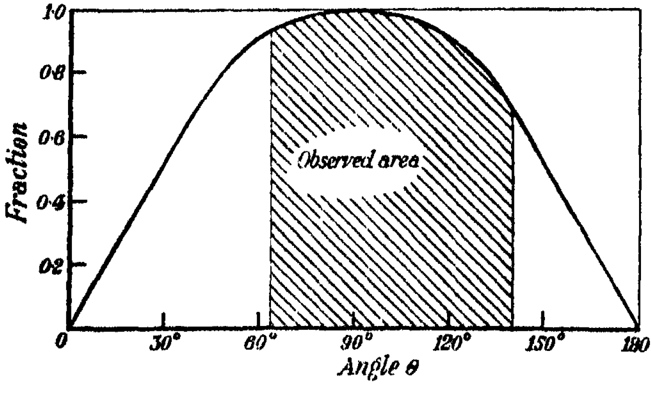

Fig. 3.—Uniform distribution. Amount scattered between θ° and (θ + 1)°.

Gray* in the region 10°–30° and also by some experiments we have carried out jointly, in the range 2°–17°. Further confirmation as to order of magnitude is to be found in the observed intensity of secondary nuclear radiation produced at about 175° by the walls and floor of the room in our normal experiments on the secondary emission.

Although the measurements are distinctly in favour of an isotropic emission of the secondary " nuclear " radiations it is important to note that the reduction of these relative values to absolute determinations of ${}_{N}\kappa_{\gamma}$ introduces considerable probability of error. Thus the statement that the whole of the energy absorbed by a nucleus is re-emitted by it as secondary radiation may be in error by 20%.

§ 7. *Resonance and the Secondary Nuclear Emission.*

There are two reasons why the energy emitted and recorded in our measurements might be expected to be less than that absorbed. The secondary radiation might be expected to show internal conversion similar to ordinary γ-radiations so that a photoelectron and not a quantum might occasionally be emitted. In addition there is the possibility that, if part of the secondary γ-ray energy is emitted as a result of transitions within the nucleus and is a characteristic of that nucleus and not of the incident radiation, then the last γ-ray to be so emitted as the nucleus falls to ground level ought to resonate with all other atomic nuclei of the same element (*cf.* Kuhn†). If this occurred it would be heavily absorbed in penetrating the lead absorbers surrounding our ionization chamber and so would not have been recorded as secondary γ-radiation.

This possibility has been tested experimentally with a simple modification of the apparatus shown in fig. 1 of Part II. These modifications included (*a*) the substitution of an iron instead of a lead absorber round the ionization chamber, and (*b*) the reduction of the direct γ-ray intensity falling on the radiator by covering the source with a lead block of special design.

As a result of the experiment it was found that the lead underneath the source produced no secondary radiation, which, falling on the normal lead radiator, resonated and was scattered into the ionization chamber.‡

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* 'Proc. Roy. Soc.,' A, vol. 130, p. 524 (1931).

† 'Phil. Mag.,' vol. 8, p. 625 (1929).

‡ It would appear that a *very strong* resonance would also lead to a negative result in this experiment, for then the radiation would be so strongly re-absorbed that no appreciable quantity would emerge from the lead sheet in which it was produced.

§ 8. *Other Methods of Exciting Atomic Nuclei to Emit γ-radiation.*

The information so far obtained concerning the character of the secondary emission, while definitely unfavourable to any hypothesis so far proposed, has given no clear positive indication as to the mechanism of the interaction.

The emission of γ-radiation, besides accompanying radioactive disintegration, is now known to be associated with a variety of nuclear processes, but comparison with the present work reveals in general a marked dissimilarity. Thus the experiments of Bothe and Becker,[*] Webster,[†] and others, have shown that γ-rays are emitted when a number of elements,, viz., Li, Be, B, F, Na, Mg, Al, are bombarded by α-particles. For each element a corpuscular radiation is also observed (either protons or neutrons) and sometimes the rough values of the quantum energy and intensity of the γ-radiation at present available suggest the correlation of the γ-rays with the energy differences between pairs of proton or neutron groups resulting from the disintegration in question.

It would appear from these results that the characteristic resonance frequencies of different nuclei within a small range of atomic number may vary irregularly between $0 \cdot 5$ and $3 \cdot 0 \,.\, 10^6$ e-volts. By contrast, the secondary γ-radiation excited by ThC″ γ-rays in light elements is predominantly of $0 \cdot 5 \,.\, 10^6$ e-volts quantum energy and is characterized by a remarkably uniform progression with atomic number. Taking into account also the difficulty of reconciling the nature of the emission excited by RaC and ThC″ γ-rays on any such hypothesis, it seems clear that some mechanism must be sought of an entirely different character from the "nuclear excitation" hypothesis so far considered.

For the same reason it is very doubtful whether the close similarity between the absorption curves of the nuclear γ-radiation of lead excited by ThC″ γ-rays, and the natural γ-radiation of polonium, implies a similarity in the mode of excitation.

An even more remarkable experimental agreement, pointed out by Webster (*loc. cit.*), is that between our results and those of Slater,[‡] who observed a γ-radiation to be produced when radon α-particles fell on thin foils of lead and tin. The measurements were difficult, but a large number of experiments gave consistent results for the absorption of secondary γ-radiation up to $1 \cdot 8$ cm.

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[*] 'Z. Physik,' vol. 66, p. 289 (1930).

[†] 'Proc. Roy. Soc.,' A, vol. 136, p. 428.

[‡] 'Phil. Mag.,' vol. 42, p. 904 (1921).

of lead. The logarithmic absorption curves were approximately linear and gave the values :—

$$\text{Lead, } \mu_{Pb} = 1 \cdot 8 \text{ cm.}^{-1}$$

$$\text{Tin, } \mu_{Pb} = 2 \cdot 1 \text{ cm.}^{-1} \qquad J_{lead}/J_{tin} = 1 \cdot 6,$$

which are in strikingly good agreement with our own values for the absorption coefficients for excitation by ThC″ γ-rays over the same range of absorber thickness, and for the ratio of the initial ionizations.

When an α-particle from radon makes a head-on collision with a lead nucleus the field at the nucleus falls from maximum to half value in a time $t = 3 \,.\, 10^{-21}$ seconds, so that the chief Fourier components will be equivalent to quanta of the order of $0 \cdot 4 \,.\, 10^6$ e-volts. Since, however, $t \propto Z$, we should have expected a harder radiation from tin than from lead if the radiation were simply a "white" X-radiation. Alternatively, one might suppose that the higher frequency components ($h\nu > 2 \,.\, 10^6$ volts) were undergoing "anomalous absorption"—such a hypothesis cannot be rejected on grounds of intensity—but any explanation in terms of the "equivalent radiation" appears to be ruled out by the fact that Bothe and Becker, and later Webster using polonium α-particles could not observe any effect as great as 1% of that found by Slater. The phenomenon deserves further investigation to make certain that these peculiar results are not produced by some unknown radiation emitted by the radon.

§ 9. *Possible Relation to the Positive Electron.*

The probable connection between the secondary γ-radiation which we have been investigating and the formation and subsequent annihilation of positive electrons was first suggested by Blackett and Occhialini* at a time when positive electrons had been observed only in connection with penetrating radiation, but it has since been established beyond doubt† that positive electrons are generated by the absorption of the high energy γ-rays of ThC″.

According to the theory of Dirac these positive electrons will ultimately become annihilated in one of two ways. If annihilation with a negative electron takes place in free space, two quanta, having a total energy of $2m_0c^2$, will be produced. The quanta are not necessarily equal, but this probability is greater than any other, so that we should expect a band of radiation having a fairly well-marked maximum of intensity at $0 \cdot 5 . 10^6$ volts—in remarkable agreement with the fact that all the elements so far examined have yielded a secondary radiation of about this quantum energy as a result of the absorption of hard ThC″ γ-rays.

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* 'Proc. Roy. Soc.,' A, vol. 139, p. 699 (1933).

† Anderson, 'Science,' vol. 2, p. 432 (1933); Chadwick, 'Proc. Roy. Soc.,' A, vol. 143, p. 1 (1933); Blackett and Occhialini, *unpublished*; Meitner and Phillip, 'Naturwiss,' vol. 23, p. 467 (1933).

If, however, the positive electron becomes annihilated under such circumstances that a massive particle (*e.g.*, a nucleus) can carry away the recoil momentum, the theory indicates that the whole mass $2m_0c^2$ may be transformed into a single quantum. The relative importance of this second type of annihilation increases with the atomic number of the absorbing material. There can be little doubt that this annihilation process contributes to the "hard component" of the secondary radiation from heavy elements, since the quantum energy of this component is approximately equal to $2m_0c^2$, and the intensity relative to the soft component increases rapidly with the atomic number.

This close correspondence between the hard and soft components of the observed secondary radiations and the radiation that would be expected to result from the two annihilation processes necessitates a fuller consideration of the relation between the absorption of the primary ThC″ radiation and the resultant γ-ray emission.

A mode of interaction between quanta and the electrons in negative energy states near atomic nuclei, analogous to the ordinary "photoelectric absorption" was proposed by Dirac, and this suggestion appears to be confirmed by the experiments of Chadwick (*loc. cit.*), Blackett, and Occhialini,* who find that the positive electrons ejected by ThC″ γ-rays from a thick lead plate have an energy distribution which ends fairly sharply at about $1 \cdot 6 . 10^6$ volts. This is the value to be expected if the incident γ-ray ($h\nu = 2 \cdot 6 . 10^6$ volts) produces two particles having the same mass as an ordinary electron (equivalent to $0 \cdot 51 . 10^6$ volts each), and if those particles move on with the remainder of the energy. A quantitative treatment of this mode of interaction has been attempted by Oppenheimer and Plesset,† who obtain results for the magnitude of the interaction, and the variation with atomic number, which are in satisfactory agreement with the values of the anomalous absorption coefficient determined by direct absorption measurements. It must be noted, however, that this calculation is really only valid (and even then is only calculated approximately) when the incident γ-ray quantum energy is very large compared with $2m_0c^2$, the rest mass energy of the positive and negative electrons which are generated.

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* *Unpublished.*

† 'Phys. Rev.,' vol. 44, p. 53 (July, 1933).

Oppenheimer and Plesset find that this coefficient varies very rapidly with quantum energy above the threshold ($1 \cdot 0 \, . \, 10^6$ volts), the value at $1 \cdot 3 \, . \, 10^6$ volts being only 1/500 of that at $2 \cdot 6 \, . \, 10^6$ volts. Our observations of the absorption coefficient of the RaC γ-rays which are effective in giving rise to the emission of anomalously scattered radiation are compatible with an excitation function having these characteristics.

On the other hand, any such simple process involving the absorption of a γ-ray quantum and the production of a positive and a negative electron, combined with the subsequent annihilation of the positive electron with another negative electron, encounters a number of difficulties :—

(*a*) The ratio of the number of positive to negative electrons emerging from a thick lead plate, when irradiated by ThC″ γ-rays, appears to be about 10%. On the other hand, direct absorption measurements show that one quantum is anomalously absorbed for every four quanta undergoing Compton scattering. Although a proper comparison of these figures requires a knowledge of the angular distribution and range of the positive electrons, as well as other quantities, which we do not yet possess, it nevertheless appears difficult to reconcile these two figures.

(*b*) When a quantum of $2 \cdot 6 \, . \, 10^6$ volts is absorbed by the production of a pair of positive and negative electrons the kinetic energy associated with the electrons will, in general, be dissipated in ionization processes ; for it is well known that the negative electron loses very little energy in radiation processes, and it seems possible that the annihilation of the positive electron will usually occur towards the end of its range. Thus the amount of energy recovered in the form of γ-radiation will, on the average, be little greater than $1 \cdot 0 \, . \, 10^6$ volts, or about 40% of the absorbed energy ; whereas our observations show that, for lead, about 80% of the absorbed energy is re-radiated in the form of γ-rays.

(*c*) Although in the annihilation in free space of a positive with a negative electron the two quanta need not be of equal energy, the *mean* energy cannot be less than $0 \cdot 51 \, . \, 10^6$ volts—the rest mass of an electron.* Thus for every quantum having an energy less than this amount, there should be one quantum with a correspondingly greater energy. This is not in agreement with experiment, since for iron irradiated by RaC γ-rays, for example, we have found that in each 100 quanta of secondary radiation emitted, there is one quantum with an energy $h\nu \sim 1 \cdot 1 \, . \, 10^6$ volts, and 99 with an energy $h\nu \sim 0 \cdot 38 \, . \, 10^6$ volts, so that 98% of the quanta with energies very markedly less than $0 \cdot 51 \, . \, 10^6$ volts have no counterpart of higher energy. In addition, the weighted mean energy of the individual quanta ($0 \cdot 39 . 10^6$ volts) is in definite disagreement with the above theoretical requirement of $0 \cdot 51 . 10^6$ volts. Although this difference is not very large we regard it as significant.* For lead this discrepancy is much less pronounced since the soft component has a higher quantum energy, and the hard component is present in much greater intensity.

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* We assume that the positive and negative electrons have equal mass.

The first two of these difficulties make it appear to us that the whole of the secondary emission is not the direct result of the annihilation of the positive electrons which have been observed up to the present. These difficulties cannot be avoided by making the assumption that the positive electrons have a very high probability of annihilation in emerging from their parent atom, because this would merely serve to increase still more the disagreement found in (*c*).

Since the above difficulties make it very probable that the anomalous absorption and emission cannot be explained completely by a simple process of the production and annihilation of a single positive electron, we have considered the possibility that these particles are produced in pairs. Such an assumption does not encounter the same difficulties concerning the total intensity of the secondary radiation or the total number of secondary quanta produced since, for each quantum absorbed, the total kinetic energy of the whole four particles produced will be only $(2 \cdot 62 - 4 \times 0 \cdot 51) = 0 \cdot 58 . 10^6$ volts and, correspondingly, at least $2 \cdot 0 . 10^6$ volts must be radiated, since each positive electron will produce two secondary quanta.

It is possible that particles with such small energy might have escaped detection in the Wilson chamber experiments, so we have looked for them with an ionization chamber of suitable dimensions. The experiment was not pushed to the limits of accuracy, but it was clear from the measurements that such particles were not present in the numbers to be expected.

§ 10. *Conclusion.*

Since it seems possible that further theoretical explanations of the "nuclear interaction of γ-radiation"—possibly on the basis of the positive electron—will shortly be advanced, it is convenient to give a short résumé of the experimental facts concerning the phenomenon. For this reason we are presenting here all of our experimental knowledge concerning the interaction which was not published in the "conclusion" of our previous paper.

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* The accuracy with which absorption coefficients have been measured and interpreted is discussed fully in Part II.

The interaction of γ-radiation with atomic nuclei, first recorded by Tarrant,* was investigated at the same time by Meitner and Hupfeld† and by Chao.‡ More complete papers have also appeared by Meitner and Hupfeld,† Jacobsen§ and by Tarrant* and have shown fair agreement over the experimental facts.

Since the total absorption of this γ-radiation varies smoothly with atomic number it follows that the nuclear absorption also does not exhibit irregularities. The experimental results indicate a variation per nucleus, nearly as the square of the atomic number (limits $Z^{2\cdot1}$ and $Z^{1\cdot8}$), but they are not sufficiently accurate to discriminate between a variation which is a simple function of the atomic number, the atomic weight or the number of α-particles in the nucleus.

The absolute value of the absorption coefficient per nucleus of this radiation ($h\nu = 2\cdot6 \times 10^6$ e-volts) for certain elements are given in Table V. The value given for a heavy element such as lead may be affected by any departure of the photoelectric effect from the experimental empirical curve of Gray.|| At the other extreme with elements of low atomic number the value is made uncertain by the possibility of the variation of the Compton scattering from the Klein and Nishina formula (due either to an inapplicability of the formula or to the inhomogeneity of the radiation), since the nuclear effect is here a small fraction of the total absorption.

Table V.

Element.	Lead.	Tin.	Iron.	Carbon.
$_N\kappa \times 10^{+27}$	2880	860	260	21
Effective radius of nucleus $\times 10^{+13}$ cm.	9·6	5·2	2·9	0·8
Usual nuclear radius $\times 10^{+13}$ cm.	7·7	—	~6	~3

The effective size of the nucleus to γ-radiation shown in Table V is calculated on the assumption that the γ-radiation is localized in a point and that interaction occurs whenever this point passes within the effective radius of the nucleus.

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* 'Proc. Roy. Soc.,' A, vol. 128, p. 345 (1930); vol. 135, p. 223 (1932).

† 'Naturwiss.,' vol. 22, p. 534 (1930); 'Z. Physik,' vol. 67, p. 147 (1931); 'Phys. Z.,' vol. 31, p. 947 (1930).

‡ 'Proc. Nat. Acad. Sci. Wash.,' vol. 16, p. 431 (1930).

§ 'Z. Physik,' vol. 170, p. 145 (1931).

|| 'Proc. Camb. Phil. Soc.,' vol. 27, p. 103 (1931).

The experiments described in the present paper show that the whole (within 10–15%) of the energy of the high frequency γ-radiation which is absorbed by a nucleus is re-emitted by it as secondary radiation and that this obtains for all elements investigated with thorium C″ radiation. This secondary radiation has been shown to consist mainly of a radiation of energy rather less than $\frac{1}{2} \times 10^6$ e-volts, so that from four to six secondary quanta of low energy radiation are produced for each quantum of high energy absorbed. Although this result follows accurately only if the radiation is emitted isotropically or according to a Thomson formula, yet experiments have shown that this assumption of isotropic emission is justified between 60° and 145°, and it is important to note that as much as 65% of the absorbed energy has actually been observed in this angular range. The possibilities of inaccuracies in the approximate isotropic distribution of the secondary radiation can therefore only affect the remainder, 35% of the total energy absorbed.

When RaC γ-radiations are employed it is not possible to determine accurate values for ${}_{N}\kappa_{\gamma}$ or for the ratio of the emitted to the absorbed energy, since we are very uncertain which lines of the γ-ray spectrum are concerned in the interaction, and the calculation can only be carried out on the assumption that the whole of the high energy radiation of RaC is participating in the phenomenon. Moreover, it is a little doubtful if the secondary emission can be analysed into two components alone, and we pointed out that the absorption curve is quite compatible with the view that a third and still softer component is present in addition to the components produced by the thorium C″ γ-radiation. Since, however, we can be confident only of the approximate identity of the hard component in the two sources, one cannot be sure that the soft components are not complicated mixtures of many different γ-ray lines emitted in different intensities by different elements so as to simulate an increasing nett hardness of the total soft component with increasing atomic number, and it is best for the purpose of the calculation of ${}_{N}\kappa_{\gamma}$ to regard the secondary radiation as made up of two components only.

For lead the value of ${}_{N}\kappa_{\gamma}$ for the soft components was found to be 1880×10^{-27}, which is in moderate agreement with that obtained by Stahel and Ketelaar (1380×10^{-27}). The hard component of the secondary radiation had a value of ${}_{N}\kappa_{\gamma}$ of 132×10^{-27} and this again is of the order of magnitude found by Stahel and Ketelaar (311×10^{-27}), and also by Meitner and Hupfeld (500×10^{-27}) who, however, did not investigate the soft component of the radiation.

We wish to express our thanks to Lord Rutherford and to Dr. Chadwick for their helpful advice throughout the investigation, and to acknowledge our indebtedness to the Council of Trinity College for a Grant from the Rouse Ball Fund covering the cost of the radiothorium employed. One of us (G. T. P. T.) desires to express his thanks to the Department of Scientific and Industrial Research for the opportunity to carry out this research.

Bombardment of the Heavy Isotope of Hydrogen by α-Particles.

By Lord Rutherford, O.M., F.R.S., and A. E. Kempton, B.A.

(Received January 18, 1934.)

The constitution of the heavy isotope of hydrogen,* of mass 2, raises a number of interesting questions on which there is at present considerable difference of opinion. We know that the nuclear charge of this element is 1, and its atomic mass has been accurately determined by Bainbridge† as 2·0136, using his modified form of mass spectrograph. As regards the actual structure of the nucleus, a number of possibilities must be considered. In the first place the nucleus may be a primary unit or composite. And secondly, if the diplon is composite it may consist either of two protons and a negative electron, or, as seems more probable, of a proton and a neutron closely combined.‡

From a consideration of the general evidence of the transformations which give rise to neutrons, Chadwick§ concludes that the mass of the neutron in the free state is 1·0067. The sum of the masses of the neutron and hydrogen atom (1·0078) is 2·0145, while the observed mass of diplogen is 2·0136, indicating that the binding energy of the combination is somewhat less than 1 million electron volts. From other considerations Curie and Joliot‖ have suggested that the neutron may have a mass as high as 1·012. On the other hand, Lawrence* concludes that the mass of the neutron may be as low as 1·0006. This value is deduced from observations on the transformation of a number of elements by bombardment with fast diplons. With many elements he observed the ejection of a proton group of about 18 cm. range, and considers that these are produced by the breaking up of the diplon, in the strong nuclear field of the transformed atom, into a neutron and a proton. In order to reconcile his observations with the principle of the conservation of energy, it is necessary to assume that the mass of the neutron is much smaller than the value deduced by Chadwick, and in fact very nearly equal to unity. On Lawrence's view, the diplon is a nucleus of an unusual type, for it possesses about 5 million volts of excess energy, which can be released under appropriate conditions.

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* The names "diplogen" for the new isotope and "diplon" for its nucleus were suggested in the Discussion on Heavy Hydrogen at the Royal Society, December 14, 1933 (see 'Proc. Roy. Soc.,' A, vol. 144 (1934)).

† 'Phys. Rev.,' vol. 44, p. 57 (1933).

‡ In a recent letter to 'Nature,' vol. 133, p. 24 (January 6, 1934) Lea has described experiments suggesting that the neutron unites with hydrogen to form diplogen, a penetrating γ-radiation being emitted in the process.

§ Bakerian Lecture, 'Proc. Roy. Soc.,' A, vol. 142, p. 14 (1933).

‖ 'J. Phys. Rad.,' vol. 4, p. 500 (1933).

There is, therefore, considerable conflict of opinion as to the structure of the diplon and the mass of the neutron. In order to throw further light on these questions, we have made experiments to test whether neutrons are liberated when diplogen is bombarded by fast α-particles. For this purpose, a layer of heavy water (containing more than 91% diplogen) was exposed to the α-rays from a source of polonium corresponding to about 10 millicuries. The heavy water was placed in a cavity, about 1 mm. deep, on a microscope slide, and the polonium source mounted directly above at about 3 mm. from the surface of the liquid. Source and water were then placed above and close to, a large ionization chamber filled with hydrogen. The ionization chamber was connected in the usual way with a valve amplifier and oscillograph. The presence of neutrons was examined by counting the number of "kicks" produced in the oscillograph, using photographic recording. The natural effect in this chamber without the polonium present gave about one throw every 2 minutes. With the source present, but no heavy water, this was raised slightly, presumably owing to radiation from the glass walls of the vessel containing the source and the microscope slide used for holding the water. No certain change in the number of kicks was observed when the heavy water used was replaced by ordinary water, or in fact when no water was used at all. The counting was done over a period of about 15 hours, alternately with heavy and ordinary water in position.

Thus with ordinary water, 233 kicks were observed in a period of 436 minutes, *i.e.*, an average of 267 kicks in 500 minutes. With heavy water the corresponding figures were 235 kicks in 430 minutes, *i.e.*, an average of 273 kicks in 500 minutes. The difference between the two sets of observations is well within the probability error, so that no definite result can be deduced. When the experiment was completed, a sheet of beryllium was exposed to the same polonium source under similar conditions, and the number of kicks per minute produced by the neutrons from the beryllium was about 10. It is therefore evident that if neutrons are produced at all in heavy water, the efficiency of production is certainly less than 1/100 of that for beryllium. Since about 1 in 10^5 α-particles is effective in liberating a neutron from beryllium, we can say that the corresponding efficiency for heavy water is certainly less than 1 in 10^7.*

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* Lawrence, Henderson and Livingston, 'Phys. Rev.,' vol. 44, p. 781 (1933).

If the postulated breaking up of a diplon into a proton and a neutron does occur, it is clearly a very rare occurrence under our experimental conditions. It can be deduced that not more than 1 in 100 violent collisions of the α-particle with the diplon is effective in disintegrating it.† It may be that the chance of an α-particle of energy about 5×10^6 e.v. disrupting a diplon of negative potential about 1×10^6 e.v. is very small, and so difficult to detect. Moreover, there is also the possibility that the α-particle may occasionally unite with the diplon to form a lithium atom of mass 6, thus,

$${}_1D^2 + {}_2He^4 \longrightarrow {}_3Li^6.$$

If such an event be possible, it is easily shown, by consideration of the masses of these atoms, as determined by Aston and Bainbridge, and the conservation of momentum, that it would take place with the liberation of about 3 million volts of excess energy. This presumably would be radiated for the most part in the form of penetrating γ-rays.‡

We are much indebted to Dr. Chadwick for his help in these experiments. He not only prepared for us a suitable polonium source, but also allowed us to make use of his apparatus specially designed for the detection of slow neutrons.

It should be possible to push these experiments further by using stronger sources of polonium and a counting chamber with the lowest possible natural effect. Such experiments would well repay their performance in giving a more definite decision on the problem involved.

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* Similar experiments have been made by Dunning and Pegram with negative results (' Bull. Amer. Phys. Soc.,' December 7, 1933).

† A brief account of these conclusions was given by Lord Rutherford in the Discussion on Heavy Hydrogen at the Royal Society, December 14, 1933.

‡ Mr. D. E. Lea, of the Cavendish Laboratory, has recently made experiments to test whether γ-rays arise in such a transformation, using a high pressure ionization chamber and polonium as a source of α-particles. No certain difference in the ionization current was observed when heavy water in place of ordinary water was bombarded by the particles.

Scattering and Absorption of α-particles by Diplogen.

The retardation of α-particles in passing through a gas is almost entirely due to the ionization of the atoms in the path. Since the ionization potential of the heavy isotope of hydrogen should be almost identical with that of ordinary hydrogen, the ionization produced by the α-particles, and consequently the stopping power for the α-particles, should be the same in the two gases. Using the apparatus described later, we have verified that the stopping power of the α-particles from polonium in a nearly pure preparation of diplogen is the same as that in ordinary pure hydrogen, viz., about 0·22 of that of air at the same pressure and temperature.

In a head-on collision of an α-particle of mass M with a particle of mass m, the velocity of recoil u of the struck particle is given by

$$u = \frac{2\mathrm{M}}{\mathrm{M} + m} \cdot \mathrm{V},$$

where V is the initial velocity of the α-particle.

In the case of collisions in ordinary hydrogen, where $m = 1$, protons will be ejected with velocity $u = 8/5\mathrm{V}$, whereas for collisions in diplogen, the diplons will recoil with a velocity of $4/3\mathrm{V}$ or 5/6 of the velocity of the proton under similar conditions. On the other hand, the energy of the recoiling diplon is 25/18 times the energy of the recoiling proton.* For the same velocity of the particles the loss of energy of the proton and diplon in traversing unit path of a gas should be the same and should vary in the same way with change of velocity. The relative ranges of the recoiling proton and diplon can be calculated from the data given by Blackett† on the variation of proton range with velocity, remembering that the range of the diplon is twice as great as that of a proton of the same initial velocity. In this way it can be shown‡ that the recoiling diplon, despite its lower initial velocity, has a range about 8% greater than the recoiling proton, when the α-rays are those from polonium of velocity $\mathrm{V} = 1 \cdot 60 \times 10^9$ cm./sec. These deductions have been completely verified in the experiments referred to later, indicating the essential correctness of the underlying assumption on which the calculations are based.

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* If greater accuracy be desired, the correct relative masses of these nuclei should be used.

† 'Proc. Roy. Soc.,' A, vol. 135, p. 132 (1932).

‡ We made use in these calculations of the range-velocity curve obtained by Blackett's method and given by Duncanson (Ph.D. Thesis, 1933) from a careful consideration of the latest data on the ranges of α-rays.

The scattering of α-particles in their passage through a gas is most conveniently studied by examining the variation of the number of recoil nuclei appearing at different angles with the direction of the incident α-particle. For hydrogen, this was done very thoroughly, many years ago, by Chadwick and Bieler.* They found that the number of recoil protons in the forward direction, *i.e.*, for small angles, was much greater than the number calculated on the assumption of an inverse law of force between the α-particle and the proton. This difference they found to be well marked even for the comparatively slow α-particles ejected from polonium.

As only about 10 c.c. of diplogen were available at the time for experiment, it was not possible to carry out a complete examination of the scattering at different angles as in the experiments of Chadwick and Bieler. A simple arrangement requiring only about 5 c.c. of diplogen was used to examine whether or not there was any marked difference between the scattering of α-particles in hydrogen or diplogen.

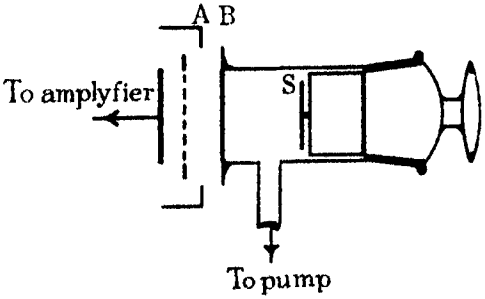

Fig. 1.

The essential features of the arrangement are shown in fig. 1. A glass tube, about 5 cm. long and 15 mm. diameter, was covered at one end with a thin brass plate, 0·5 mm. thick, perforated with 100 holes, each of diameter 0·49 mm. Over this was waxed a mica sheet of stopping power equivalent to 1·94 cm. of air. The other end was a ground glass joint through which was introduced the polonium source, deposited on a disc about 8 mm. in diameter. When in position the source was 2 cm. distant from the mica plate. The apparatus was air tight and could be exhausted or filled with the gas under examination by means of a suitable pump. The source of polonium had an activity equal to about 3 mg. radium. The diplogen used, for the preparation of which we are indebted to Dr. Harteck, was freed from oxygen and nitrogen by heating a tungsten wire in the presence of the vapour from a supply of heavy water containing more than 98% diplogen. An ordinary ionization chamber α-ray counter connected to a valve amplifier was used to count the number of recoil particles, either photographically, or, when the numbers were small, near the end of the range of the particles, by telephone. For the smallest absorption used the number of recoil particles varied from 100 to 200 per minute in different experiments. Mica absorbers were placed between A and B and the variation in number of the particles from hydrogen and diplogen was carefully observed for thicknesses of the absorber greater than the range of the α-particles. The results, for both gases, are shown in fig. 2. It will be seen that the two curves are very similar in shape over the whole range of absorption. The maximum range of the diplons was found to be 18·3 cm., about 7% greater than that of the protons (17·1 cm.), under the same conditions.* The increased number of diplons for each absorption is about

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* 'Phil. Mag.,' vol. 42, p. 923 (1921), or Rutherford, Chadwick, and Ellis, "Radiations from Radioactive Substances," p. 256 (1930).

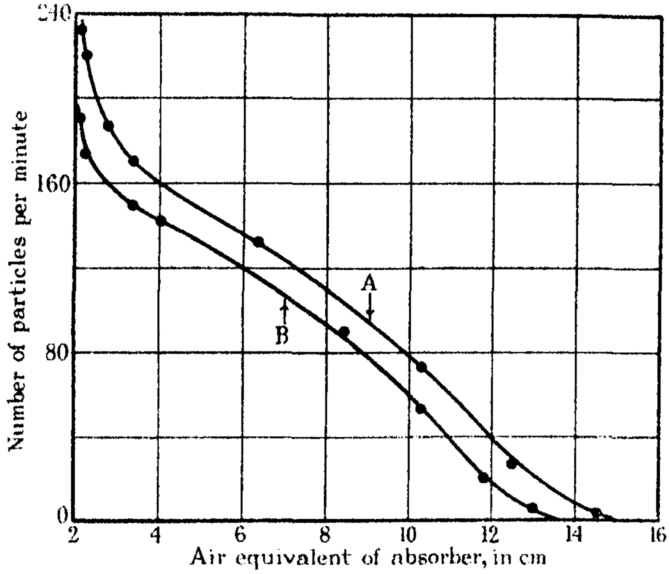

FIG. 2.—A, diplogen; B, hydrogen.

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* The experiments were not designed to measure accurately the maximum range of the protons projected by the α-particles from a clean preparation of polonium. This is given by Blackett as 17·3 cm., whereas Duncanson's data give the slightly higher value of 17·47 cm.

that to be expected from the increased range of travel of the diplons, if the field of force which gives rise to the scattering is not very different for both the isotopes of hydrogen.

There is no evidence that any considerable fraction of the collisions in diplogen leads to the disruption of the diplogen nucleus, for this would show itself in a decrease in the number of fast recoil particles and a consequent increase in the number of slower ones. We may conclude therefore, from these experiments, that the field of force surrounding the diplogen nucleus must be sensibly the same as for the hydrogen nucleus, within the limits involved in this experiment.

A more complete examination of the scattering at different angles using α-particles of greater energy might disclose some difference in the fields of force for very close collisions, for it is unlikely that the fields of force of the diplon and proton would be identical at very small distances.

We desire to express our thanks to Mr. G. R. Crowe for helping in these experiments. One of us (A. E. K.) is indebted for a grant from the Department of Scientific and Industrial Research.

Summary.

(1) Experiments have been made to test whether the diplon can be broken up into a neutron and proton in the bombardment of diplogen by the α-particles from polonium. No certain evidence was obtained of the production of neutrons when heavy water was bombarded by α-particles. The number of neutrons, if any, was certainly less than 1 in 10^7 of the number of bombarding α-particles.

(2) The maximum range of recoil in air of the diplon in a head-on collision with an α-particle from polonium is about 7% greater than that of recoil of the proton. This is in agreement with calculations based on observed data with the proton. As is to be expected, the stopping power of the α-particle is the same in diplogen as in hydrogen.

(3) The scattering of α-particles by diplogen was compared with the scattering of α-particles by hydrogen. Apart from the greater range of travel of the diplon under similar conditions of recoil, no certain difference could be detected by our experimental method. It is concluded that the field of force surrounding the diplon is sensibly the same as that of the proton.

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